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Theory and interpretation of pressure-induced resonances

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(Received 18 July 1988)

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Using both a bare-atom and dressed-atom picture of atom-field interactions, we present a theory of the pressure-induced resonances that can arise when four radiation fields interact with a three-level quantum system. The four fields drive two coupled atomic transitions which share a common level, the levels being arranged in a "ladder" scheme. As the field frequencies are varied, certain resonant structures in the excitation spectrum of the upper state population appear only in the presence of collisions. The resonant structures result from processes that have been referred to in the past as collisionally aided radiative excitation (CARE) and pressure-induced extra resonances in four-wave mixing (PIER4). We show that both CARE- and PIER4-type resonances have a common origin, which can be linked to conservation of energy. In contrast to conventional PIER4 signals, line shapes calculated in this work result from a "single atom" rather than a collective emission. Moreover, the signals vanish unless the applied fields are relatively coherent, again in contrast to conventional PIER4.

I. INTRODUCTION

Spectroscopic line shapes provide us with most of the data we have concerning atomic level spacings and atomic-state lifetimes. In an atomic vapor, the spectroscopic line shapes are modified as a result of collisions occurring within the vapor. The most commonly known effect of this type is the so-called pressure broadening of spectral lines, in which absorption or emission lines are broadened as a result of collisions. Perhaps somewhat less familiar is a whole series of processes in which collisions result in new structure in either linear or nonlinear spectroscopic line shapes.

The collision-induced features can occur in reactions in which both colliding atoms change their internal states as a result of the combined collisional-radiative interaction.¹ They can also occur when a forbidden transition becomes allowed as a result of collisions.² In this paper, neither of these cases is discussed. Instead, we consider the interaction of atoms with one or more radiation fields that drive allowed transitions in these "active" atoms. The active atoms undergo collisions with ground-state perturber atoms which remain in their ground state and interact negligibly with the radiation fields. Nevertheless, the active atom-perturber collisions can modify the active atom-radiation field interaction in a manner that leads to new features in the absorption and emission line shapes.

Collisional effects of this nature have been broadly divided into two categories. The first category can be termed collisionally aided radiative excitation (CARE),³ and is illustrated in Fig. 1. A weak laser field having frequency Ω drives a transition between the ground state 1 and excited state 2 of an active atom. The magnitude of the detuning $\Delta = \omega - \Omega$ (ω = 1-2 transition frequency) is larger than the decay rate of level 2. A second weak laser

has its frequency Ω' tuned in the neighborhood of the 2-3 transition frequency ω' and the population of state 3, ρ_{33} , is monitored as a function of $\Delta' = \omega' - \Omega'$. In the absence of collisions, there is a single resonance centered at $\Delta' = -\Delta$ ($\Omega' + \Omega = \omega + \omega'$). When collisions occur, however, there is an additional resonance centered at $\Delta' = 0$ ($\Omega' = \omega'$).⁴ This type of collision-induced feature can also be observed in fluorescence, where it goes under the name of *collisional redistribution*.⁵ In that case, the fluorescence spectrum from level 2 consists of a single peak centered at the laser frequency Ω in the absence of collisions. With collisions present, there is an additional peak centered at the atomic transition frequency ω . In both cases above, the width of the additional component is determined by the decay rate of the optical coherence associated with the transition levels. A physical explanation of these CARE resonances is given in Sec. II. At this point, however, we note that, since the collision-induced features are monitored from atomic state populations, they are essentially "single atom" effects. No cooperative emission is needed.

The second category of collision-induced features occurs for the atom-field interaction indicated in Fig. 2. Two laser fields having frequencies Ω and $\Omega + \delta$ drive the 1-2 transition. These fields result in a modulation of the population of state 2 at rate δ . When a third field is applied having frequency Ω , it is possible to obtain a four-wave-mixing signal which propagates with frequency $\Omega - \delta$. For detunings $|\Delta| = |\omega - \Omega|$ much larger than the natural width of the 1-2 transition (and any Doppler widths), it is found that, as δ is varied, a resonant structure centered at $\delta = 0$ having width [full width at half maximum (FWHM)] $2\gamma_2$ appears in the signal field *only* in the presence of collisions. Such pressure-induced extra resonances in four-wave mixing (PIER4) were predicted

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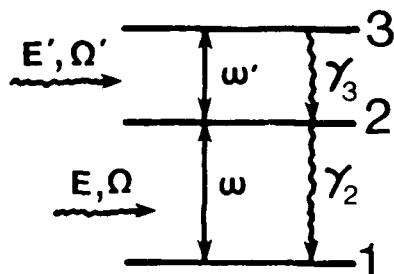


FIG. 1. Energy-level scheme for collisionally aided radiative excitation (CARE). The detuning $\Delta = \omega - \Omega$ is held fixed as the detuning $\Delta' = \omega' - \Omega'$ is varied. The upper state population excitation spectrum has a resonant structure centered at $\Delta' = 0$ only in the presence of collisions.

and observed by Bloembergen and co-workers.^{6,7} They differ from the first category of resonances in that their width is determined by an atomic-state population decay rate rather than a coherence decay rate. Moreover, as observed in four-wave mixing, they result from a cooperative phase-matched coherent emission.

It is the purpose of this paper to compare the two categories of resonances and to examine the origin of both categories of resonances using a unified approach. As such, we will show that PIER4-type resonances can be observed using level schemes similar to that shown in Fig. 1. In other words, the PIER signals can be observed as a single atom effect rather than in cooperative emission. Moreover, the signals which are calculated for the level scheme of Fig. 1 will be seen to depend on the relative coherence of the applied laser fields, in contrast to the conventional PIER4 signals.

This paper is organized as follows. In Sec. II a physical description of both CARE and PIER4 is given and similarities and differences between the two categories of resonances are noted. In Sec. III we use a three-level atom and four laser fields to derive a signal that possesses

both CARE- and PIER4-type features. The common origin of both resonant structures emerges in this section. The calculation in Sec. III is carried out using a semiclassical approach. In Sec. IV this calculation is repeated using a fully quantized, dressed-atom approach. It is argued that the pressure-induced resonances can be explained on the basis of conservation of energy. In planned companion papers, we shall investigate pressure-induced signals which arise in (a) the fluorescence beats emitted by a two-level atom driven by two laser fields; (b) the excitation of a "four-level" atom using four applied laser fields; and (c) the two-photon ionization of an atom produced using two laser fields. In those papers a semiclassical dressed-atom picture will be introduced which provides an alternative approach for carrying out the calculations than the methods developed herein.

II. DISCUSSION OF PRESSURE-INDUCED EXTRA RESONANCES (PIER)

In this section we show that the pressure-induced extra resonances observed in collisionally aided radiative excitation (CARE) and four-wave mixing (PIER4) are interrelated. The existence of both of these pressure-induced extra resonances can be traced to a collisional interaction in which part of the internal energy of the (active-atom plus radiation field) is transformed into translational energy of the colliding atoms. Both a standard "bare-atom" picture and a dressed-atom picture is used to illustrate this aspect of the theory. It is always assumed that level 1 is the ground state and that collisions alone are insufficiently energetic to cause transitions between the internal atomic states under consideration.

A. CARE

The level scheme for a typical CARE reaction is shown in Fig. 1. One laser has its frequency Ω held fixed at a value which gives a detuning $|\Delta| = |\omega - \Omega|$ that is large compared with the natural and Doppler widths associated with the 1-2 transition, but small or comparable to the inverse duration of a collision. The Rabi frequency associated with this field, which drives the 1-2 transition only, is denoted by χ ($\chi = \mu_{12} E / 2\hbar$; μ_{12} is the dipole moment matrix element, E is the field amplitude). A second laser field (frequency Ω' ; Rabi frequency $\chi' = \mu_{23} E' / 2\hbar$) drives the 2-3 transition only. As the detuning $\Delta' = \omega' - \Omega'$ is varied, the population of state 3 is monitored. In this, as well as in all subsequent discussions, *it is assumed that the laser fields are weak*; results are calculated to lowest non-vanishing order in the field amplitudes.

A question that may be posed is for what detunings Δ' does resonant excitation of level 3 occur? The answer to this question at first appears to be paradoxical. Consider first a density-matrix treatment of the problem. Two types of density-matrix chains lead from an initial population ρ_{11} to a final population ρ_{33} (ρ_{ij} is the $i-j$ density-matrix element). The first of these involves the intermediate state population ρ_{22} , and can be represented schematically as

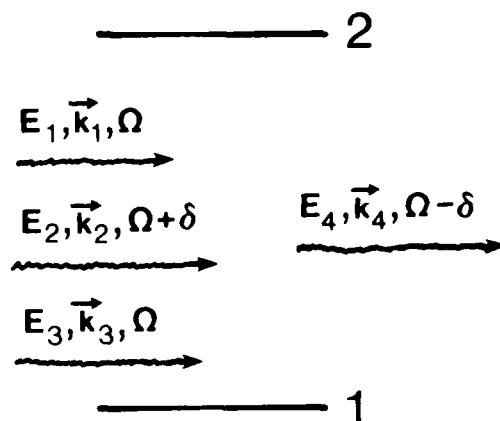
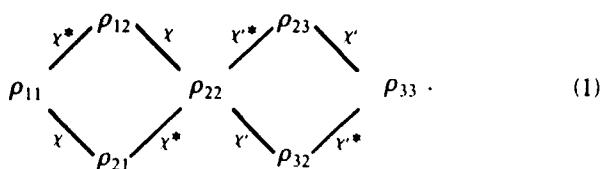
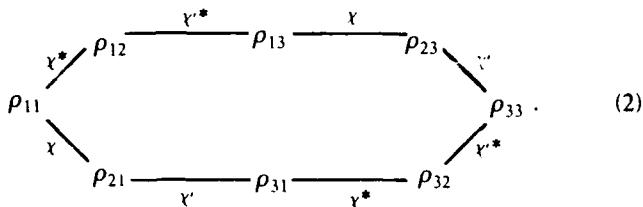


FIG. 2. A four-wave-mixing signal having wave propagation vector $\mathbf{k}_4 = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$ and frequency $\Omega_4 = \Omega - \delta$ is produced when three fields having propagation vectors $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3$ and frequencies $\Omega_1 = \Omega, \Omega_2 = \Omega + \delta, \Omega_3 = \Omega$ drive a two-level atomic transition. A resonant structure in the signal intensity centered at $\delta = 0$ appears only in the presence of collisions [pressure-induced extra resonance in four wave mixing (PIER4)].



The Rabi frequencies in chain (1) specify the field that produces a given density-matrix element from a preceding one in a perturbative solution to the problem. For chain (1), which can be referred to as a stepwise (SW) chain, the population ρ_{33} varies as $|\chi|^2|\chi'|^2$. Moreover, the excitation appears as the sequential absorption of a photon from field 1 and 2 photon from field 2. Consequently, there should be a resonance centered at $\Delta' = \omega' - \Omega' = 0$ for the second step in the absorptive process.

The second perturbative chain leading to a contribution to ρ_{33} of order $|\chi|^2|\chi'|^2$ is represented schematically by the chain



This chain can be termed a two-quantum (TQ) chain since it requires the simultaneous action of both fields. The presence of ρ_{13} (or ρ_{31}) in the chain indicates a two-quantum resonance condition $\Omega + \Omega' = \omega + \omega'$ (or $\Delta + \Delta' = 0$). Thus, from a density-matrix approach, there appears to be two resonances, a $\Delta' = 0$ resonance from chain (1) and a $\Delta' = -\Delta$ resonance from chain (2).

On the other hand, consider what happens if the probability amplitude of state 3 is calculated. In an amplitude picture, state 2 is coupled to state 1 by field χ and state 3 to state 2 by field χ' . When the amplitude calculation is carried out (and all transients have died away), only the two-quantum resonance ($\Delta' = -\Delta$) remains. There seems to be a paradox—one resonance from an amplitude approach and two from a density-matrix approach.

The resolution of this paradox lies in the limited applicability of the amplitude approach. The amplitude argument given above is valid only in the absence of collisions. If collisions occur, the state amplitudes undergo rapid phase changes at the time of the collision, leading to new contributions for the final-state population. It is easier to incorporate the collisional effects into the density matrix rather than the amplitude equations. Collisions result in a decay of off-diagonal density-matrix elements, with no population decay. In the amplitude picture, one must consider the role of a single collision at each active atom site, sum over the contributions to the final-state density matrix element from each site, and then average over collision histories.

The question regarding the number of resonances can now be clarified. In the absence of collisions, the amplitude approach is valid and there is a single resonance centered at $\Delta' = -\Delta$ ($\Omega + \Omega' = \omega + \omega'$). This result can be further understood by making reference to Fig. 1. The fields are assumed to be monochromatic, and absorption

of the fields occurs by atoms with a well-defined ground-state energy. Imagine for the moment that state 3 was metastable. Then owing to conservation of energy, excitation to level 3 could occur only when $\Omega + \Omega' = \omega + \omega'$, independent of the width of level 2. When level 3 has a finite width, the conclusion is not altered except that the resonance condition need be satisfied only within the natural width of level 3. The existence of a single resonance is linked to conservation of energy.⁸ How is this result explained in the density-matrix approach? It turns out that, in the absence of collisions, the TQ chain (2) contains a term which exactly cancels the $\Delta' = 0$ resonance of the SW chain (1).⁸ This result can be viewed as a destructive interference effect between the two chains.

When collisions are present, the amplitude approach discussed above is no longer valid. Moreover, is not possible to use a conservation-of-energy argument to rule out the possibility of a $\Delta' = 0$ ($\Omega' = \omega'$) centered resonance, since the colliding atoms can now compensate for the detuning Δ by a corresponding change of $\hbar\Delta$ in their translational energy. In other words, state 2 can be populated by a CARE reaction in which the energy mismatch $\hbar\Delta$ is provided by this collision. Absorption from level 2 then results in the SW resonance centered at $\Omega' = \omega'$. As a consequence of collisions, the contribution of the SW chain grows linearly with the pressure, and the $\Omega' = \omega'$ centered resonance is no longer canceled by the TQ chain. With collisions present, both the $\Delta' = 0$ and $\Delta' = -\Delta$ resonances exist.

The appearance of the $\Delta' = 0$ resonance can be viewed as the "destruction of destructive interference." The destructive interference of the SW and TQ chains, which combined to eliminate the $\Delta' = 0$ resonance of the SW contribution in the absence of collisions, is itself "destroyed" in the presence of collisions. Although such an interpretation is possible, it seems to us that the arguments relating to energy conservation offer a more physical interpretation of the results.

Up to now, we have employed what can be termed a bare-atom picture (BAP) of the excitation process. It is "bare" in the sense that eigenstates of the isolated atom are used. It will prove useful to also consider a dressed-atom picture (DAP) of the reaction.^{9,10} In the DAP, eigenstates of the atom plus the field driving the 1-2 transition serve as the basis states for the problem. In the weak-field limit, the appropriate eigenstates and eigenenergies (E_1 is arbitrarily taken equal to zero) are

$$|I\rangle = |1; n_1, n_2\rangle + \frac{\chi}{\Delta} |2; n_1 - 1, n_2\rangle, \quad E_I = 0 \quad (3a)$$

$$|II\rangle = -\frac{\chi^*}{\Delta} |1; n_1, n_2\rangle + |2; n_1 - 1, n_2\rangle, \quad E_{II} = \hbar\Delta \quad (3b)$$

$$|III\rangle = |3; n_1 - 1, n_2 - 1\rangle, \quad E_{III} = \hbar(\Delta + \Delta') \quad (3c)$$

where n_1 is the number of photons in the first field and n_2 is the number in the second. These dressed states are illustrated in Fig. 3. States |II⟩ and |III⟩ have energies $\hbar\Delta$ and $\hbar(\Delta + \Delta')$, respectively, relative to state |I⟩. As Δ' is varied, state |III⟩ moves vertically in Fig. 3, and resonances can occur whenever state |III⟩ becomes degenerate with either states |I⟩ or |II⟩.

In the absence of collisions, assuming that the field χ is

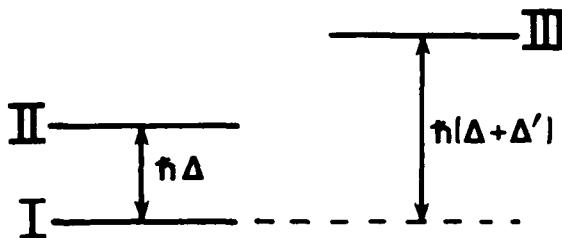


FIG. 3. Dressed-state energy levels in the weak-field limit. As Δ' is varied, the energy of state $|III\rangle$ moves vertically in the figure. Resonances can occur when $E_{III}=E_I$ (centered at $\Delta'=-\Delta$) or when $E_{III}=E_{II}$ (centered at $\Delta'=0$). In the absence of collisions, state $|II\rangle$ is not populated and only the $\Delta'=-\Delta$ resonance exists.

turned on in a time long compared with $|\Delta|^{-1}$, only dressed state $|I\rangle$ is populated. The absence of state $|II\rangle$ population is directly linked to the conservation of energy—there is no mechanism to provide the energy $\hbar\Delta$ to excite state $|II\rangle$. As a consequence, the only resonance that occurs in the absence of collisions is that for which state $|III\rangle$ is degenerate with state $|I\rangle$, i.e., when $(\Delta+\Delta')=0$. When collisions occur, the situation changes. Collisions, which do not couple the bare states, do couple dressed states $|I\rangle$ and $|II\rangle$ since each of these states is a superposition of states $|1\rangle$ and $|2\rangle$. As a result of collisions, state $|II\rangle$ is populated and a new resonance centered at $\Delta'=0$ appears when state $|III\rangle$ is degenerate with state $|II\rangle$. From either the DAP or BAP, the same conclusions are reached concerning the existence of the resonances. In both descriptions, the absence of the $\Delta'=0$ resonance can be predicted on the basis of conservation of energy arguments.

B. PIER4

Pressure-induced extra resonances have been observed using the four-wave-mixing geometry depicted schematically in Fig. 2. Instead of considering the level scheme of Fig. 2, we choose to analyze that of Fig. 4, since it is similar to that discussed above for CARE. Four fields, having Rabi frequencies ($\chi, \chi_+, \chi', \chi'_+$) and corresponding frequencies ($\Omega, \Omega+\delta, \Omega', \Omega'-\delta'$) are incident on the “three-level” atom shown in Fig. 4. Fields χ and χ_+ drive the 1-2 transition only and fields χ' and χ'_+ drive the 2-3 transition only. The detuning $|\Delta|$ is much larger than the natural width of level 2 (and also larger than the Doppler width associated with the 1-2 transition frequency), while the detuning $|\delta|$ is comparable with the decay rate γ_2 of level 2. In the general case to be considered in Sec. III, both δ and δ' can be varied. For the present discussion, however, δ' is set equal to δ .

The frequencies are chosen to satisfy an “energy-conservation” condition that is analogous to that of conventional four-wave mixing. In the PIER4 experiments, three fields are incident having frequencies $\Omega_1=\Omega$, $\Omega_2=\Omega+\delta$, $\Omega_3=\Omega$. The generated field has a frequency Ω_4 whose frequency is derived from the energy-conservation condition

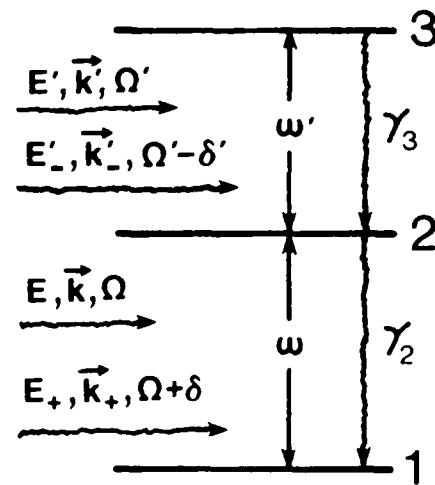


FIG. 4. Energy-level diagram and field configuration for observing pressure-induced extra resonances via a four-wave-mixing interaction. Four fields are incident on the “three-level” atom as shown. Fields E and E_+ drive the 1-2 transition and fields E' and E'_+ drive the 2-3 transition. As the population of level 3 is monitored for fixed Ω and Ω' , a resonant structure centered at $\delta=0$ appears in the excitation spectrum only when collisions are present.

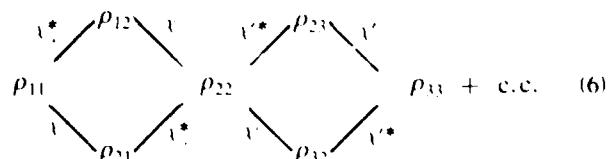
$$\Omega_4 = \Omega_1 + \Omega_3 - \Omega_2 = \Omega - \delta . \quad (4)$$

[The fields must also satisfy momentum conservation $\mathbf{k}_4 = \mathbf{k}_1 + \mathbf{k}_3 - \mathbf{k}_2$ (\mathbf{k}_i is the propagation vector for field i) and phase matching, $k_4 = \Omega_4/c$.] If, in Fig. 4, we associate fields 1, 2, and 3 with the fields having frequencies $\bar{\Omega}_1 = \Omega$, $\bar{\Omega}_2 = \Omega + \delta$, $\bar{\Omega}_3 = \Omega'$, respectively, then the fourth field $\bar{\Omega}_4 = \Omega' - \delta$ satisfies

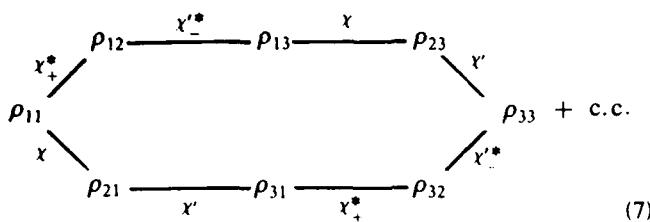
$$\bar{\Omega}_4 = \bar{\Omega}_1 + \bar{\Omega}_3 - \bar{\Omega}_2 = \Omega' - \delta , \quad (5)$$

in analogy with Eq. (4). Thus, our fields satisfy an equation similar to the energy-conservation condition of four-wave mixing. As will be seen below, however, the fact that the fields are chosen to satisfy an energy-conservation condition does not invalidate the conclusion that pressure-induced extra resonances can be explained in terms of conservation of energy arguments as was done above for CARE.

The discussion parallels that given for CARE. We first adopt a bare-atom approach (BAP). In this section we consider only the contribution to ρ_{33} (Fig. 4) proportional to the product of the four Rabi frequencies of the fields. The two perturbation chains which give rise to this contribution are



and



As in CARE, the SW chain (6) leads to resonant structures in ρ_{33} whenever Ω' [or $(\Omega' - \delta)$] is equal to ω' .¹¹ Moreover, there is a new resonant structure that appears centered at $\delta=0$ having width $2\gamma_2$. This resonance can be viewed as arising from an interference between the two pathways leading to ρ_{22} in chain (6). The TQ chain contains the two-photon resonance centered at $\Omega + \Omega' = \omega + \omega'$, having width γ_3 . In the absence of collisions, however, the resonant structures at $\Omega' = \omega'$, $(\Omega' - \delta) = \omega'$, and $\delta = 0$ of the SW chain are exactly canceled by the TQ chain, just as in CARE.

This result can again be explained using an amplitude rather than density-matrix approach. Using probability amplitudes, one calculates the upper state amplitude as the sum of four terms, each representing a two-photon transition to state 3 which varies as the product of a lower (χ or χ_+) and upper (χ' or χ_-) field Rabi frequency. Since each term contains two-photon resonance conditions only, when the amplitude is squared, the resultant upper state population ρ_{33} exhibits resonances only when $(\Omega, \Omega + \delta) + (\Omega', \Omega' - \delta) = \omega + \omega'$. This amplitude argument is valid only if collisions are absent. Once collisions occur, this amplitude argument fails and one finds that the SW chain resonances at $\Omega' = \omega'$, $\Omega' - \delta = \omega'$, and $\delta = 0$ are not totally canceled by the TQ chain (7). Since the vanishing of the SW resonances is implicitly linked to the absence of a collision channel in which internal (atom + field) energy can be transformed into translational energy of the colliding atoms, we again see that the absence of PIER can be associated with conservation of energy. This conclusion is strengthened if the reaction is viewed using a dressed-atom approach (DAP).

In the DAP there are now seven relevant atom-field states,

$$\begin{aligned} & |1; n_1, n_2; n_3, n_4\rangle, |2; n_1 - 1, n_2; n_3, n_4\rangle, \\ & |2; n_1, n_2 - 1; n_3, n_4\rangle, |3; n_1 - 1, n_2; n_3 - 1, n_4\rangle, \\ & |3; n_1 - 1, n_2; n_3, n_4 - 1\rangle, |3; n_1, n_2 - 1; n_3 - 1, n_4\rangle, \\ & |3; n_1, n_2 - 1; n_3, n_4 - 1\rangle, \end{aligned}$$

where the photon numbers refer to fields $\chi, \chi_+, \chi', \chi_-$ respectively. The fields χ and χ_+ are considered as the "dressing" fields. In the weak-field limit, the eigenkets and eigenenergies of the (atom + dressing fields) system are given by

$$\begin{aligned} |\mathcal{A}\rangle &= |1; n_1, n_2; n_3, n_4\rangle + \frac{\chi}{\Delta} |2; n_1 - 1, n_2; n_3, n_4\rangle \\ &+ \frac{\chi_+}{\Delta - \delta} |2; n_1, n_2 - 1; n_3, n_4\rangle, E_{\mathcal{A}} = 0, \end{aligned} \quad (8a)$$

$$|\mathcal{B}\rangle = -\frac{\chi^*}{\Delta} |1; n_1, n_2; n_3, n_4\rangle + |2; n_1 - 1, n_2; n_3, n_4\rangle \quad (8b)$$

$$E_{\mathcal{B}} = \hbar\Delta;$$

$$|\mathcal{C}\rangle = -\frac{\chi^*}{\Delta - \delta} |1; n_1, n_2; n_3, n_4\rangle + |2; n_1, n_2 - 1; n_3, n_4\rangle \quad (8c)$$

$$E_{\mathcal{C}} = \hbar(\Delta - \delta),$$

along with the remaining eigenkets and eigenenergies

$$|\mathcal{4}\rangle = |3; n_1 - 1, n_2; n_3 - 1, n_4\rangle, E_4 = \hbar(\Delta + \Delta') \quad (8d)$$

$$|\mathcal{5}\rangle = |3; n_1 - 1, n_2; n_3, n_4 - 1\rangle, E_5 = \hbar(\Delta + \Delta' + \delta) \quad (8e)$$

$$|\mathcal{6}\rangle = |3; n_1, n_2 - 1; n_3 - 1, n_4\rangle, E_6 = \hbar(\Delta + \Delta' - \delta) \quad (8f)$$

$$|\mathcal{7}\rangle = |3; n_1, n_2 - 1; n_3, n_4 - 1\rangle, E_7 = \hbar(\Delta + \Delta'). \quad (8g)$$

For the moment, we consider transitions to final states $|\mathcal{4}\rangle$ and $|\mathcal{7}\rangle$ only (a method for isolating these terms is discussed in Secs. III and IV). The appropriate energy level diagram is shown in Fig. 5.

In the absence of collisions, owing to conservation of energy, dressed states $|\mathcal{B}\rangle$ and $|\mathcal{C}\rangle$ are unoccupied, so that transitions to states $|\mathcal{4}\rangle$ and $|\mathcal{7}\rangle$ must originate in state $|\mathcal{A}\rangle$. As δ is varied the energies of states $|\mathcal{A}\rangle$, $|\mathcal{4}\rangle$, and $|\mathcal{7}\rangle$ remain unchanged. Consequently, there can be no resonant structure centered at $\delta = 0$. Note that this result is now directly related to conservation of energy, since the absence of population in states $|\mathcal{B}\rangle$ and $|\mathcal{C}\rangle$ is a consequence of energy conservation.

When collisions occur, states $|\mathcal{B}\rangle$ and $|\mathcal{C}\rangle$ are populated and a coherence is created between these states. We must now consider the combined effect of the $A \rightarrow 4, 7$, $B \rightarrow 4, 7$, and $C \rightarrow 4, 7$ transitions. As δ is varied, a resonant structure in the ρ_{33} excitation spectrum is observed

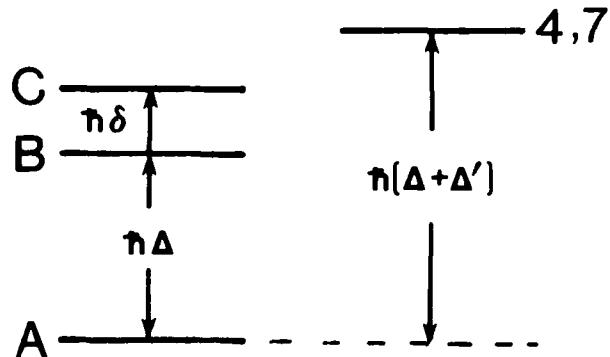


FIG. 5. Energy-level diagram for some of the dressed states associated with the atom-field interaction of Fig. 4. Fields \mathbf{E} and \mathbf{E}_+ serve as the dressing fields. States $|\mathcal{4}\rangle$ and $|\mathcal{7}\rangle$ (which are degenerate when $\delta' = \delta$) correspond to states in which the atom is in level 3. For fixed Δ and Δ' , excitation to states $|\mathcal{4}\rangle$ and $|\mathcal{7}\rangle$ occurs in the wings of the $A \rightarrow 4, 7$, $B \rightarrow 4, 7$, and $C \rightarrow 4, 7$ transitions, as shown. In the absence of collisions, only state $|\mathcal{A}\rangle$ is populated. With collisions present, states $|\mathcal{B}\rangle$ and $|\mathcal{C}\rangle$ are populated and a B - C coherence is produced. As δ is varied, a "level-crossing" resonance centered at $\delta = 0$ appears in the excitation spectrum of states $|\mathcal{4}\rangle$ and $|\mathcal{7}\rangle$, resulting from the collision-induced creation of the B - C coherence.

centered at $\delta=0$ having width $2\gamma_2$. The $\delta=0$ resonance can be viewed as a level crossing of states $|B\rangle$ and $|C\rangle$ in the DAP.¹⁰ The intensity of this level-crossing resonance is proportional to the magnitude of the coherence ρ_{BC} , which vanishes (along with ρ_{BB} and ρ_{CC}) in the absence of collisions.

To conclude this section, we comment briefly on conventional PIER4 for two-level atoms. In PIER4, energy conservation is seemingly built in since condition (4) is satisfied. Two "pump" photons, each having frequency Ω are transformed into a probe and signal photon having frequencies $(\Omega+\delta)$ and $(\Omega-\delta)$, respectively. However, as we have seen above, although energy is conserved for the fields' photons, it does not rule out an explanation based on energy-conservation arguments. If a DAP is used, the dressed states $|A\rangle$, $|B\rangle$, and $|C\rangle$ are still as indicated in Fig. 5. What we plan to show in a future work is that the PIER4 signal can be interpreted as a stimulated Raman transition between states $|B\rangle$ and $|C\rangle$ with the third field (at frequency Ω) providing the Raman pump to produce a Stokes field at frequency $(\Omega-\delta)$. The physical arguments relating to the origin of the PIER4 resonances in such a stimulated Raman scattering would then be analogous to those presented above for three-level atoms interacting with four fields.

III. CALCULATION OF PIER SIGNAL: BARE-ATOM APPROACH

An explicit calculation of the PIER signal for the level scheme of Fig. 4 is now given. The calculation is first carried out using a semiclassical theory (classical fields, quantum-mechanical atoms) and is then repeated using a fully quantized approach.

Four fields are incident on atoms in an atomic vapor having the energy-level structure shown in Fig. 4. The first two fields, which are nearly resonant with the 1-2 transition, have electric field vectors given by

$$\mathbf{E}(\mathbf{R}, t) = \frac{1}{2} \hat{\mathbf{e}} E e^{i(\mathbf{k} \cdot \mathbf{R} - \Omega t)} + \text{c.c.}, \quad (9a)$$

$$\mathbf{E}_+(\mathbf{R}, t) = \frac{1}{2} \hat{\mathbf{e}}_+ E_+ e^{i[\mathbf{k}_+ \cdot \mathbf{R} - (\Omega + \delta)t]} + \text{c.c.}, \quad (9b)$$

where $\hat{\mathbf{e}}, \hat{\mathbf{e}}_+$ are (complex) unit polarization vectors, E, E_+ are (complex) field amplitudes, \mathbf{k}, \mathbf{k}_+ are field propagation vectors, $\Omega, (\Omega + \delta)$ are the field frequencies, and c.c. stands for "complex conjugate." The second two fields, which are nearly resonant with the 2-3 transition, have electric field vectors given by

$$\mathbf{E}'(\mathbf{R}, t) = \frac{1}{2} \hat{\mathbf{e}}' E' e^{i(\mathbf{k}' \cdot \mathbf{R}' - \Omega' t)} + \text{c.c.}, \quad (9c)$$

$$\mathbf{E}'_-(\mathbf{R}, t) = \frac{1}{2} \hat{\mathbf{e}}'_- E'_- e^{i[\mathbf{k}'_- \cdot \mathbf{R}' - (\Omega' - \delta')t]} + \text{c.c.} \quad (9d)$$

The difference between the 1-2 and 2-3 transition frequencies, denoted by ω and ω' , respectively, is sufficiently large to insure that fields \mathbf{E} and \mathbf{E}_+ drive the 1-2 transition only and fields \mathbf{E}' and \mathbf{E}'_- drive the 2-3 transition only.

The calculation is carried out in terms of atomic density-matrix elements ρ_{ij} whose time development is given by

$$i\hbar\dot{\rho}_{ij} = [H, \rho]_{ij} + (\partial\rho_{ij}/\partial t)_{\text{relaxation}}, \quad (10)$$

where

$$H = H_0 + V \quad (11)$$

is the Hamiltonian for the system without relaxation. The quantity H_0 is the free-atom Hamiltonian and V is the atom-field interaction Hamiltonian taken to be of the form

$$V = -\mu \cdot \mathbf{E}_T(\mathbf{R}, t), \quad (12)$$

where μ is the atomic dipole moment operator and \mathbf{E}_T is the total electric field, that is, a sum of the four fields given in Eq. (9). The time derivative in Eq. (10) is to be interpreted as a total time derivative equal to $\partial/\partial t + \mathbf{v} \cdot \nabla$.

To account for relaxation, we adopt a rather simple (but adequate) model to incorporate the effects of spontaneous emission and collisions. As a result of spontaneous emission, level 2 decays to level 1 at rate γ_2 and level 3 to level 2 at rate γ_3 . Collisions with ground-state buffer gas atoms are assumed to affect active-atom level coherences only, leading to a decay rate $\Gamma_{ij} = \Gamma_{ji}$ for the density-matrix element ρ_{ij} ($i \neq j$). The rate Γ_{ij} is proportional to the buffer gas pressure. Recall that level 1 is the ground state, $\gamma_1 = 0$.

When the relaxation terms are included in Eq. (10), and an interaction representation defined by

$$\rho_{12} = \tilde{\rho}_{12} e^{-i(\mathbf{k} \cdot \mathbf{R} - \Omega t)}, \quad (13a)$$

$$\rho_{23} = \tilde{\rho}_{23} e^{-i(\mathbf{k}' \cdot \mathbf{R} - \Omega' t)}, \quad (13b)$$

$$\rho_{13} = \tilde{\rho}_{13} e^{-i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{R} - (\Omega + \Omega')t}, \quad (13c)$$

$$\tilde{\rho}_{ij} = \tilde{\rho}_{ji}^*, \quad (13d)$$

is introduced, one finds density-matrix elements which evolve as

$$\begin{aligned} \partial\rho_{22}/\partial t + \mathbf{v} \cdot \nabla \rho_{22} = & -\gamma_2 \rho_{22} + \gamma_3 \rho_{33} - i(\chi^* \tilde{\rho}_{21} - \chi \tilde{\rho}_{12}) - i(\chi'_+ e^{-i(\mathbf{k}' \cdot \mathbf{R} - \delta t)} \tilde{\rho}_{21} - \chi'_- e^{i(\mathbf{k}' \cdot \mathbf{R} - \delta t)} \tilde{\rho}_{12}) \\ & - i(\chi' \tilde{\rho}_{23} - \chi'^* \tilde{\rho}_{32}) - i(\chi'_- e^{i(\mathbf{k}' \cdot \mathbf{R} + \delta' t)} \tilde{\rho}_{23} - \chi'^* e^{-i(\mathbf{k}' \cdot \mathbf{R} + \delta' t)} \tilde{\rho}_{32}), \end{aligned} \quad (14a)$$

$$\partial\rho_{33}/\partial t + \mathbf{v} \cdot \nabla \rho_{33} = -\gamma_3 \rho_{33} + i(\chi' \tilde{\rho}_{23} - \chi'^* \tilde{\rho}_{32}) + i(\chi'_- e^{i(\mathbf{k}' \cdot \mathbf{R} + \delta' t)} \tilde{\rho}_{23} - \chi'^* e^{-i(\mathbf{k}' \cdot \mathbf{R} + \delta' t)} \tilde{\rho}_{32}), \quad (14b)$$

$$\begin{aligned} \partial\tilde{\rho}_{12}/\partial t + \mathbf{v} \cdot \nabla \tilde{\rho}_{12} = & -[(\gamma_{12} + \Gamma_{12}) - i(\Delta + \mathbf{k} \cdot \mathbf{v})] \tilde{\rho}_{12} + i\chi^* (\rho_{22} - \rho_{11}) + i\chi'_+ e^{-i(\mathbf{k}' \cdot \mathbf{R} - \delta t)} (\rho_{22} - \rho_{11}) \\ & - i\chi' \tilde{\rho}_{13} - i\chi'_- e^{i(\mathbf{k}' \cdot \mathbf{R} + \delta' t)} \tilde{\rho}_{13}, \end{aligned} \quad (14c)$$

$$\begin{aligned} \partial\tilde{\rho}_{23}/\partial t + \mathbf{v} \cdot \nabla \tilde{\rho}_{23} = & -[(\gamma_{23} + \Gamma_{23}) - i(\Delta' + \mathbf{k}' \cdot \mathbf{v})] \tilde{\rho}_{23} + i\chi'^* (\rho_{33} - \rho_{22}) + i\chi'^* e^{-i(\mathbf{k}' \cdot \mathbf{R} + \delta' t)} (\rho_{33} - \rho_{22}) \\ & + i\chi \tilde{\rho}_{13} + i\chi'_+ e^{i(\mathbf{k}' \cdot \mathbf{R} - \delta t)} \tilde{\rho}_{13}, \end{aligned} \quad (14d)$$

$$\begin{aligned} \partial \tilde{\rho}_{13} / \partial t + \mathbf{v} \cdot \nabla \tilde{\rho}_{13} = & -\{(\gamma_{13} + \Gamma_{13}) - i[(\Delta + \Delta') + (\mathbf{k} + \mathbf{k}') \cdot \mathbf{v}]\} \tilde{\rho}_{13} + i\chi^* \tilde{\rho}_{23} + i\chi_+^* e^{-i(\kappa \cdot \mathbf{R} - \delta t)} \tilde{\rho}_{23} \\ & - i\chi'^* \tilde{\rho}_{12} - i\chi_-^* e^{-i(\kappa' \cdot \mathbf{R} + \delta' t)} \tilde{\rho}_{12}, \end{aligned} \quad (14e)$$

where

$$\gamma_{ij} = (\gamma_i + \gamma_j)/2, \quad (15)$$

$$\chi = \langle 2|\mathbf{k}|1\rangle \cdot \hat{\mathbf{E}} / 2\hbar, \quad \chi_+ = \langle 2|\mathbf{k}|1\rangle \cdot \hat{\mathbf{E}}_+ E_+ / 2\hbar, \quad (16a)$$

$$\chi' = \langle 3|\mathbf{k}|2\rangle \cdot \hat{\mathbf{E}}' E' / 2\hbar, \quad \chi'_- = \langle 3|\mathbf{k}|2\rangle \cdot \hat{\mathbf{E}}'_- E'_- / 2\hbar \quad (16b)$$

$$\Delta = \omega - \Omega, \quad \Delta_+ = \omega - (\Omega + \delta) \quad (17a)$$

$$\Delta' = \omega' - \Omega', \quad \Delta'_- = \omega' - (\Omega' - \delta') \quad (17b)$$

$$\kappa = \mathbf{k}_+ - \mathbf{k}, \quad \kappa' = \mathbf{k}'_- - \mathbf{k}' . \quad (18)$$

In writing Eqs. (14), it is assumed implicitly that the magnitudes of all the frequencies defined in Eqs. (15)–(17) are smaller than the inverse duration of a collision (impact approximation). This assumption is needed to enable us to model collisional effects using simple decay parameters. The lower state population does not appear explicitly on the left-hand side of Eqs. (14), but is determined by the condition

$$\rho_{11} + \rho_{22} + \rho_{33} = W(\mathbf{v}), \quad (19)$$

where $W(\mathbf{v})$ is the equilibrium velocity distribution,

$$W(\mathbf{v}) = (\pi u^2)^{-3/2} e^{-v^2/u^2}, \quad (20)$$

in which u is the most probable atomic speed.

We seek a steady-state solution of Eqs. (14) for ρ_{33} to lowest nonvanishing order in the field amplitudes, corresponding to terms of order $|\chi|^2 |\chi'|^2, \chi \chi_+^* |\chi'|^2, \chi \chi_+^* \chi' \chi_-^*$, etc. In this perturbation limit, it is sufficient to consider the following truncated form of Eqs. (14):

$$\begin{aligned} \partial \rho_{22} / \partial t + \mathbf{v} \cdot \nabla \rho_{22} = & -\gamma_2 \rho_{22} - i[(\chi^* + \chi_+^* e^{-i(\kappa \cdot \mathbf{R} - \delta t)}) \tilde{\rho}_{21} \\ & - (\chi + \chi_+ e^{i(\kappa \cdot \mathbf{R} - \delta t)}) \tilde{\rho}_{12}], \end{aligned} \quad (21a)$$

$$\begin{aligned} \partial \rho_{33} / \partial t + \mathbf{v} \cdot \nabla \rho_{33} = & -\gamma_3 \rho_{33} + i[(\chi' + \chi'_- e^{i(\kappa' \cdot \mathbf{R} + \delta' t)}) \tilde{\rho}_{23} \\ & - (\chi'^* + \chi'_- e^{-i(\kappa' \cdot \mathbf{R} + \delta' t)}) \tilde{\rho}_{32}], \end{aligned} \quad (21b)$$

$$\begin{aligned} \partial \tilde{\rho}_{12} / \partial t + \mathbf{v} \cdot \nabla \tilde{\rho}_{12} = & -(\gamma_{12}' - i\tilde{\Delta}) \tilde{\rho}_{12} \\ & - i(\chi^* + \chi_+^* e^{-i(\kappa \cdot \mathbf{R} - \delta t)}) W(\mathbf{v}), \end{aligned} \quad (21c)$$

$$\begin{aligned} \partial \tilde{\rho}_{23} / \partial t + \mathbf{v} \cdot \nabla \tilde{\rho}_{23} = & -(\gamma_{23}' - i\tilde{\Delta}') \tilde{\rho}_{23} - i(\chi'^* + \chi'_- e^{-i(\kappa' \cdot \mathbf{R} + \delta' t)}) \rho_{22} \\ & + i(\chi + \chi_+ e^{i(\kappa \cdot \mathbf{R} - \delta t)}) \tilde{\rho}_{13}, \end{aligned} \quad (21d)$$

$$\begin{aligned} \partial \tilde{\rho}_{13} / \partial t + \mathbf{v} \cdot \nabla \tilde{\rho}_{13} = & -[\gamma_{13}' - i(\tilde{\Delta} + \tilde{\Delta}')] \tilde{\rho}_{13} \\ & - i(\chi'^* + \chi'_- e^{-i(\kappa' \cdot \mathbf{R} + \delta' t)}) \tilde{\rho}_{12}, \end{aligned} \quad (21e)$$

where

$$\gamma_{12}' = \frac{1}{2} \gamma_2 + \Gamma_{12}, \quad \gamma_{23}' = \gamma_{23} + \Gamma_{23}, \quad \gamma_{13}' = \frac{1}{2} \gamma_3 + \Gamma_{13} \quad (22)$$

$$\tilde{\Delta} = \Delta + \mathbf{k} \cdot \mathbf{v}, \quad \tilde{\Delta}' = \Delta + \mathbf{k}' \cdot \mathbf{v}. \quad (23a)$$

For future reference, we also define

$$\tilde{\Delta}_+ = \Delta_+ + \mathbf{k}_+ \cdot \mathbf{v}, \quad \tilde{\Delta}'_- = \Delta'_- + \mathbf{k}'_- \cdot \mathbf{v} \quad (23b)$$

$$\tilde{\delta} = \delta - \kappa \cdot \mathbf{v}, \quad \tilde{\delta}' = \delta' + \kappa' \cdot \mathbf{v}, \quad (24)$$

where Δ_+ and Δ'_- are defined in Eqs. (17). In writing Eqs. (21), we set $\rho_{11} = W(\mathbf{v})$; higher-order corrections to ρ_{11} lead to contributions to ρ_{33} which are down by order $|\chi|^2$ from those calculated in this work.

To first order in the fields, it follows from Eq. (21c) that $\tilde{\rho}_{12}$ can be written as

$$\tilde{\rho}_{12} = \tilde{\rho}_{12}(\tilde{\Delta}) + \tilde{\rho}_{12}(\tilde{\Delta}_+) e^{-i(\kappa \cdot \mathbf{R} - \delta t)}. \quad (25)$$

When Eq. (25) is substituted into Eq. (21c), one finds steady-state values

$$\tilde{\rho}_{12}(\tilde{\Delta}) = -i\chi^* W(\mathbf{v}) / (\gamma_{12}' - i\tilde{\Delta}), \quad (26a)$$

$$\tilde{\rho}_{12}(\tilde{\Delta}_+) = -i\chi_+^* W(\mathbf{v}) / (\gamma_{12}' - i\tilde{\Delta}_+). \quad (26b)$$

Having obtained $\tilde{\rho}_{12}$ (along with $\tilde{\rho}_{21} = \tilde{\rho}_{12}^*$), we proceed to calculate ρ_{22} and $\tilde{\rho}_{13} = \tilde{\rho}_{31}^*$ which are needed as intermediate steps in a perturbative calculation of ρ_{33} [see, for example, chains (6) and (7)].

To second order in the fields, it follows from Eqs. (21a) and (25) that the population ρ_{22} can be written

$$\rho_{22} = \rho_{22}(0) + \rho_{22}(\tilde{\delta}) e^{-i(\kappa \cdot \mathbf{R} - \delta t)} + [\rho_{22}(\tilde{\delta})]^* e^{i(\kappa \cdot \mathbf{R} - \delta t)}, \quad (27)$$

which, when substituted into Eq. (21a), may be combined with Eqs. (13d) and (22)–(26) to give

$$\rho_{22}(0) = \frac{2\gamma_{12}'}{\gamma_2} \left[\frac{|\chi|^2}{(\gamma_{12}')^2 + \tilde{\Delta}^2} + \frac{|\chi_+|^2}{(\gamma_{12}')^2 + \tilde{\Delta}_+^2} \right] W(\mathbf{v}), \quad (28a)$$

$$\rho_{22}(\tilde{\delta}) = \frac{\chi \chi_+^* W(\mathbf{v})}{(\gamma_{12}' - i\tilde{\Delta}_+) (\gamma_{12}' + i\tilde{\Delta})} \left[1 + \frac{2\Gamma_{12}}{\gamma_2 + i\tilde{\delta}} \right]. \quad (28b)$$

Similarly, to second order in the fields, it follows from Eqs. (21e) and (25) that $\tilde{\rho}_{13}$ can be written as

$$\begin{aligned} \tilde{\rho}_{13} = & \tilde{\rho}_{13}(\tilde{\Delta} + \tilde{\Delta}') + \tilde{\rho}_{13}(\tilde{\Delta}_+ + \tilde{\Delta}') e^{-i(\kappa \cdot \mathbf{R} - \delta t)} \\ & + \tilde{\rho}_{13}(\tilde{\Delta} + \tilde{\Delta}'_-) e^{-i(\kappa' \cdot \mathbf{R} + \delta' t)} \\ & + \tilde{\rho}_{13}(\tilde{\Delta}_+ + \tilde{\Delta}'_-) e^{-i[(\kappa + \kappa') \cdot \mathbf{R} - (\delta - \delta') t]}, \end{aligned} \quad (29)$$

which, combined with Eqs. (21e) and (22)–(26), yields

$$\tilde{\rho}_{13}(\tilde{\Delta} + \tilde{\Delta}') = \frac{-\chi^* \chi'^* W(\mathbf{v})}{[\gamma_{13}' - i(\tilde{\Delta} + \tilde{\Delta}')](\gamma_{12}' - i\tilde{\Delta})}, \quad (30a)$$

$$\tilde{\rho}_{13}(\tilde{\Delta}_+ + \tilde{\Delta}') = \frac{-\chi_+^* \chi'^* W(v)}{[\gamma'_{13} - i(\tilde{\Delta}_+ + \tilde{\Delta}')] (\gamma'_{12} - i\tilde{\Delta}_+)} , \quad (30b)$$

$$\tilde{\rho}_{13}(\tilde{\Delta} + \tilde{\Delta}'_-) = \frac{-\chi^* \chi'^* W(v)}{[\gamma'_{13} - i(\tilde{\Delta} + \tilde{\Delta}'_-)] (\gamma'_{12} - i\tilde{\Delta})} , \quad (30c)$$

$$\tilde{\rho}_{13}(\tilde{\Delta}_+ + \tilde{\Delta}'_-) = \frac{-\chi_+^* \chi'^* W(v)}{[\gamma'_{13} - i(\tilde{\Delta}_+ + \tilde{\Delta}'_-)] (\gamma'_{12} - i\tilde{\Delta}_+)} . \quad (30d)$$

The next step is to calculate $\tilde{\rho}_{23} = \tilde{\rho}_{32}^*$. To third order in the fields, it follows from Eqs. (21d), (27), and (29) that $\tilde{\rho}_{23}$ can be written

$$\begin{aligned} \tilde{\rho}_{23} = & \tilde{\rho}_{23}(\tilde{\Delta}') + \tilde{\rho}_{23}(\tilde{\Delta}'_-) e^{-i(\kappa' \cdot \mathbf{R} + \delta' t)} + \tilde{\rho}_{23}(\tilde{\Delta}' - \tilde{\delta}) e^{-i(\kappa \cdot \mathbf{R} - \delta t)} + \tilde{\rho}_{23}(\tilde{\Delta}' + \tilde{\delta}) e^{i(\kappa \cdot \mathbf{R} - \delta t)} \\ & + \tilde{\rho}_{23}(\tilde{\Delta}'_- - \tilde{\delta}) e^{-i[(\kappa + \kappa') \cdot \mathbf{R} - (\delta - \delta') t]} + \tilde{\rho}_{23}(\tilde{\Delta}'_- + \tilde{\delta}) e^{i[(\kappa - \kappa') \cdot \mathbf{R} - (\delta + \delta') t]} . \end{aligned} \quad (31)$$

When this is substituted into Eq. (21d) and Eqs. (27) and (29) are used, one may obtain

$$\tilde{\rho}_{23}(\tilde{\Delta}') = \frac{-i\chi'^* \rho_{22}(0) + i\chi \tilde{\rho}_{13}(\tilde{\Delta} + \tilde{\Delta}') + i\chi_+ \tilde{\rho}_{13}(\tilde{\Delta}_+ + \tilde{\Delta}')}{\gamma'_{23} - i\tilde{\Delta}'} , \quad (32a)$$

$$\tilde{\rho}_{23}(\tilde{\Delta}'_-) = \frac{-i\chi'^* \rho_{22}(0) + i\chi \tilde{\rho}_{13}(\tilde{\Delta} + \tilde{\Delta}'_-) + i\chi_+ \tilde{\rho}_{13}(\tilde{\Delta}_+ + \tilde{\Delta}'_-)}{\gamma'_{23} - i\tilde{\Delta}'_-} , \quad (32b)$$

$$\tilde{\rho}_{23}(\tilde{\Delta}' - \tilde{\delta}) = \frac{-i\chi'^* \rho_{22}(\tilde{\delta}) + i\chi \tilde{\rho}_{13}(\tilde{\Delta}_+ + \tilde{\Delta}')}{\gamma'_{23} - i(\tilde{\Delta}' - \tilde{\delta})} , \quad (32c)$$

$$\tilde{\rho}_{23}(\tilde{\Delta}' + \tilde{\delta}) = \frac{-i\chi'^* \rho_{22}(\tilde{\delta})^* + i\chi_+ \tilde{\rho}_{13}(\tilde{\Delta} + \tilde{\Delta}'_-)}{\gamma'_{23} - i(\tilde{\Delta}' + \tilde{\delta})} , \quad (32d)$$

$$\tilde{\rho}_{23}(\tilde{\Delta}'_- - \tilde{\delta}) = \frac{-i\chi'^* \rho_{22}(\tilde{\delta}) + i\chi \tilde{\rho}_{13}(\tilde{\Delta}_+ + \tilde{\Delta}'_-)}{\gamma'_{23} - i(\tilde{\Delta}'_- - \tilde{\delta})} , \quad (32e)$$

$$\tilde{\rho}_{23}(\tilde{\Delta}'_- + \tilde{\delta}) = \frac{-i\chi'^* \rho_{22}(\tilde{\delta})^* + i\chi_+ \tilde{\rho}_{13}(\tilde{\Delta} + \tilde{\Delta}'_-)}{\gamma'_{23} - i(\tilde{\Delta}'_- + \tilde{\delta})} , \quad (32f)$$

which are to be combined with Eqs. (28) and (30).

Finally, we calculate ρ_{33} . To fourth order in the fields, it follows from Eqs. (21b) and (31) that ρ_{33} can be written as

$$\begin{aligned} \rho_{33} = & \rho_{33}(0) + \rho_{33}(\tilde{\delta}) e^{-i(\kappa \cdot \mathbf{R} - \delta t)} \\ & + \rho_{33}(\tilde{\delta}') e^{i(\kappa' \cdot \mathbf{R} + \delta' t)} \\ & + \rho_{33}(\tilde{\delta} - \tilde{\delta}') e^{-i[(\kappa + \kappa') \cdot \mathbf{R} - (\delta - \delta') t]} \\ & + \rho_{33}(\tilde{\delta} + \tilde{\delta}') e^{-i[(\kappa - \kappa') \cdot \mathbf{R} - (\delta + \delta') t]} + \text{c.c.} \end{aligned} \quad (33)$$

If Eq. (30) is substituted into Eq. (21), and Eq. (31) is used, one can obtain

$$\rho_{33}(0) = \frac{1}{\gamma_3} [i\chi' \tilde{\rho}_{23}(\tilde{\Delta}') + i\chi'_- \tilde{\rho}_{23}(\tilde{\Delta}'_-)] , \quad (34a)$$

$$\begin{aligned} \rho_{33}(\tilde{\delta}) = & \frac{1}{\gamma_3 + i\tilde{\delta}} \{ i\chi' \tilde{\rho}_{23}(\tilde{\Delta}' - \tilde{\delta}) - i\chi'^* [\tilde{\rho}_{23}(\tilde{\Delta}' + \tilde{\delta})]^* \\ & + i\chi'_- \tilde{\rho}_{23}(\tilde{\Delta}'_- - \tilde{\delta}) \\ & - i\chi'^* [\tilde{\rho}_{23}(\tilde{\Delta}'_- + \tilde{\delta})]^* \} , \end{aligned} \quad (34b)$$

$$\rho_{33}(\tilde{\delta}') = \frac{i\chi'_- \tilde{\rho}_{23}(\tilde{\Delta}') - i\chi'^* [\tilde{\rho}_{23}(\tilde{\Delta}'_-)]^*}{\gamma_3 + i\tilde{\delta}'} , \quad (34c)$$

$$\rho_{33}(\tilde{\delta} - \tilde{\delta}') = \frac{i\chi' \tilde{\rho}_{23}(\tilde{\Delta}' - \tilde{\delta}) - i\chi'^* [\tilde{\rho}_{23}(\tilde{\Delta}' + \tilde{\delta}')]^*}{\gamma_3 + i(\tilde{\delta} - \tilde{\delta}')} , \quad (34d)$$

$$\rho_{33}(\tilde{\delta} + \tilde{\delta}') = \frac{i\chi'_- \tilde{\rho}_{23}(\tilde{\Delta}' - \tilde{\delta}) - i\chi'^* [\tilde{\rho}_{23}(\tilde{\Delta}'_- + \tilde{\delta})]^*}{\gamma_3 + i(\tilde{\delta} + \tilde{\delta}')} , \quad (34e)$$

which is to be combined with Eqs. (32), (28), and (30).

Equations (25)–(34) are quite general. By combining these equations, it is possible to show that $\rho_{33}(0)$ has terms which vary as $|\chi\chi'|^2$, $|\chi_+\chi'|^2$, $|\chi\chi'_-|^2$, $|\chi_+\chi'_-|^2$, that $\rho_{33}(\tilde{\delta})$ has terms which vary as $\chi\chi'_+|\chi'|^2$ or $\chi\chi'_+|\chi'_-|^2$, that $\rho_{33}(\tilde{\delta}')$ has terms which vary as $|\chi|^2\chi'_-\chi'^*$ or $|\chi_+|^2\chi'_-\chi'^*$; that $\rho_{33}(\tilde{\delta} - \tilde{\delta}')$ varies as $\chi\chi'_+\chi'\chi'^*$, and that $\rho_{33}(\tilde{\delta} + \tilde{\delta}')$ varies as $\chi\chi'_+\chi'^*\chi'$. In this paper we are concerned only with the contribution to ρ_{33} that varies as the product of the four distinct field amplitudes. Experimentally, this contribution could be isolated by field modulation techniques. The contributions to ρ_{33} which vary as the product of the four amplitudes are represented by the terms $\rho_{33}(\tilde{\delta} - \tilde{\delta}')$ and $\rho_{33}(\tilde{\delta} + \tilde{\delta}')$ in Eq. (34) (plus their conjugates) [see also chains (6) and (7)]. It is possible to render the $\rho_{33}(\tilde{\delta} + \tilde{\delta}')$ contribution negligible by choosing an appropriate phase-matching condition. If the wave vectors $\mathbf{k}, \mathbf{k}', \mathbf{k}_+, \mathbf{k}_-$, and frequencies δ and δ'

are chosen such that

$$\kappa = \mathbf{k}_+ - \mathbf{k} = -\kappa' = -(\mathbf{k}'_+ - \mathbf{k}'), \quad (35a)$$

$$\delta = \delta', \quad (35b)$$

and if, in addition,

$$|\kappa L| \gg 1 \text{ or } |\delta t_{\text{obs}}| \gg 1, \quad (36)$$

where L is the cell length and t_{obs} is some observation time in the experiment, the contribution to ρ_{33} from the

$\rho_{33}(\delta + \delta')$ component, which varies as $\exp\{-i[(\kappa - \kappa') \cdot \mathbf{R} - (\delta + \delta')t]\}$ [see Eq. (33)] goes to zero when averaged over the cell length or observation time. In what follows, we assume that conditions (35) and (36) are valid, and we calculate

$$S(\delta) = \rho_{33}(\delta - \delta) + [\rho_{33}(\delta - \delta)]^*. \quad (37)$$

From Eqs. (34d), (32e), (32d), (28), (30a), (30d), (35), (23), and (24), one finds

$$\begin{aligned} S(\delta) = & \frac{\chi\chi^* + \chi'\chi'^* W(\mathbf{v})}{\gamma_3(\gamma'_{12} - i\bar{\Delta}_+)(\gamma'_{12} + i\bar{\Delta})} \\ & \times \left\{ \left[2\Gamma_{12} \left[1 + \frac{2\Gamma_{23} + \gamma_3}{\gamma_2 + i\delta} \right] / [(\gamma'_{23} + i\bar{\Delta}'_-)(\gamma'_{23} - i\bar{\Delta}')] \right] + \frac{(2\Gamma_{13} + \gamma_3)}{(\gamma'_{13})^2 + (\bar{\Delta} + \bar{\Delta}')^2} \right. \\ & \left. + (\Gamma_{13} + \Gamma_{12} - \Gamma_{23}) \left[\frac{1}{[\gamma'_{13} - i(\bar{\Delta} + \bar{\Delta}')](\gamma'_{23} - i\bar{\Delta}')} + \frac{1}{[\gamma'_{13} + i(\bar{\Delta} + \bar{\Delta}')](\gamma'_{23} + i\bar{\Delta}'_-)} \right] \right\} + \text{c.c.} \end{aligned} \quad (38)$$

One notes immediately that, in the absence of collisions ($\Gamma_{ij} = 0$), only the two-photon resonance centered at $\bar{\Delta} + \bar{\Delta}' = 0$ remains, a result that was predicted in Sec. II on the basis of conservation of energy arguments. When collisions occur, CARE-type resonances centered at $\bar{\Delta}' = 0$, $\bar{\Delta}'_- = 0$, as well as a PIER4-type resonance centered at $\delta = 0$, appear. If a PIER4-type resonance exists, it necessarily follows that a CARE-type resonance also exists. This interdependence reflects the common origin of the two processes.

To examine the resonance centered at $\delta = 0$, we consider the limit of large detunings for fields \mathbf{E} and \mathbf{E}_+ , such that

$$|\Delta| \simeq |\Delta_+| \simeq |\bar{\Delta}| \simeq |\bar{\Delta}_+| \gg \kappa u. \quad (39)$$

Moreover, we take $\Delta' = 0$ in order to maximize the signal, and limit δ to values

$$|\delta| \leq \gamma_2 \ll \kappa u, \quad (40)$$

With these values of detunings, the second and third terms of Eq. (38) (and their conjugates) can be neglected and one finds a velocity-averaged signal (denoted by $\langle \dots \rangle$),

$$\begin{aligned} \langle S(\delta) \rangle = & \frac{\chi\chi^* + \chi'\chi'^*}{\gamma_3 \Delta^2} \\ & \times \int d\mathbf{v} \left[\frac{W(\mathbf{v})}{[\gamma'_{23} + i(\mathbf{k}'_+ \cdot \mathbf{v} + \delta)](\gamma'_{23} - i\mathbf{k}' \cdot \mathbf{v})} \right. \\ & \left. \times 2\Gamma_{12} \left[1 + \frac{\gamma_3 + 2\Gamma_{23}}{\gamma_2 + i(\delta - \kappa \cdot \mathbf{v})} \right] \right] \\ & + \text{c.c.} \end{aligned} \quad (41)$$

To avoid any significant residual Doppler broadening of the $\delta = 0$ resonance, one must arrange to have

$$\kappa u \ll \gamma_2, \quad (42)$$

which can be satisfied for nearly parallel beams [the beams must be *slightly* misaligned to satisfy inequality (36)]. When inequality (42) holds, one finds

$$\begin{aligned} \langle S(\delta) \rangle = & \frac{\chi\chi^* + \chi'\chi'^*}{\gamma_3 \Delta^2} \\ & \times \int d\mathbf{v} \left[\frac{W(\mathbf{v})}{[\gamma'_{23} + i(\mathbf{k}'_+ \cdot \mathbf{v} + \delta)](\gamma'_{23} - i\mathbf{k}' \cdot \mathbf{v})} \right] \\ & \times 2\Gamma_{12} \left[1 + \frac{\gamma_3 + 2\Gamma_{23}}{\gamma_2 + i\delta} \right] + \text{c.c.} \end{aligned} \quad (43)$$

At high pressures where $\Gamma_{23}/\gamma_{23} \gg 1$, for $|\delta| \leq \gamma_2$ the signal varies as

$$\langle S(\delta) \rangle \propto \frac{\chi\chi^* + \chi'\chi'^*}{\Delta^2} \frac{\Gamma_{12}\Gamma_{23}}{\gamma_2 + i\delta} + \text{c.c.}, \quad (44)$$

that is, as the square of the pressure.¹²

An important feature to note is that the signal varies as $\chi\chi^* + \chi'\chi'^*$. Thus, for a nonvanishing signal, the fields must be relatively coherent. This result is in contrast to PIER4 where the signal varies as the absolute square of the input fields.^{6,7} Since the signal calculated above depends on the field amplitudes, it is possible to adjust the relative phases of the fields to give either an absorptive or dispersive shape to the excitation profile (44).

IV. CALCULATION OF PIER SIGNAL: DRESSED-ATOM APPROACH

We now outline a dressed-atom approach (DAP) to the problem discussed in Sec. III. Each radiation field is now taken to be quantized rather than a classical field. The Hamiltonian for the system, in the rotating-wave or reso-

nance approximation (i.e., $|\Delta| \ll \omega; |\Delta'| \ll \omega'$) is

$$H = \hbar\omega\sigma_{22} + \hbar(\omega + \omega')\sigma_{33} + \sum_{j=1}^4 \hbar\Omega_j(a_j^\dagger a_j + \frac{1}{2}) - i\hbar \sum_{j=1}^4 (f_j \sigma_+^j a_j - f_j^* a_j^\dagger \sigma_-^j), \quad (45)$$

where

$$\sigma_+^1 = \sigma_+^2 = |2\rangle\langle 1|, \quad (46a)$$

$$\sigma_+^3 = \sigma_+^4 = |3\rangle\langle 2|, \quad (46b)$$

$$\sigma_-^j = (\sigma_+^j)^\dagger \quad (46c)$$

are operators that act on atomic states, a_j^\dagger and a_j are creation and annihilation operators for field mode j , and f_j is a coupling constant which is specified below. It has been assumed that each field consists of a single mode. The fields are labeled by the indices 1,2,3,4 which correspond to the fields of Fig. 4 as follows:

$$E_1(\mathbf{k}_1, \Omega_1, \bar{n}_1) = \mathbf{E}(\mathbf{k}, \Omega), \quad (47a)$$

$$E_2(\mathbf{k}_2, \Omega_2, \bar{n}_2) = \mathbf{E}_+(\mathbf{k}_+, \Omega + \delta), \quad (47b)$$

$$E_3(\mathbf{k}_3, \Omega_3, \bar{n}_3) = \mathbf{E}'(\mathbf{k}', \Omega') \quad (47c)$$

$$E_4(\mathbf{k}_4, \Omega_4, \bar{n}_4) = \mathbf{E}'_-(\mathbf{k}'_-, \Omega' - \delta'), \quad (47d)$$

where \bar{n}_i is the average number of photons in field i .

A convenient basis set consists for the kets is $|j; n_1, n_2, n_3, n_4\rangle$ where $j=1, 2, 3$ specifies the atomic state and n_i the number of photons in field i . With this set of basis kets, the Hamiltonian has an infinite number of nearly degenerate states (e.g., all states with $n_1 + n_2 = \text{const.}$ are nearly degenerate). However, in the limit of weak fields, the number of nearly degenerate states which are of importance is truncated. If our goal is to calculate ρ_{33} to lowest order, the relevant basis states and associated energies are

$$|1; n\rangle = |1; n_1, n_2, n_3, n_4\rangle, \quad E_1 = 0 \quad (48a)$$

$$|2; n\rangle = |2; n_1 - 1, n_2, n_3, n_4\rangle, \quad E_2 = \hbar\Delta \quad (48b)$$

$$|3; n\rangle = |2; n_1, n_2 - 1, n_3, n_4\rangle, \quad E_3 = \hbar(\Delta - \delta) \quad (48c)$$

$$|4; n\rangle = |3; n_1 - 1, n_2, n_3 - 1, n_4\rangle, \quad E_4 = \hbar(\Delta + \Delta') \quad (48d)$$

$$|5; n\rangle = |3; n_1 - 1, n_2, n_3, n_4 - 1\rangle, \quad E_5 = \hbar(\Delta + \Delta' + \delta') \quad (48e)$$

$$|6; n\rangle = |3; n_1, n_2 - 1, n_3 - 1, n_4\rangle, \quad E_6 = \hbar(\Delta + \Delta' - \delta) \quad (48f)$$

$$|7; n\rangle = |3; n_1, n_2 - 1, n_3, n_4 - 1\rangle, \quad E_7 = \hbar(\Delta + \Delta' + \delta' - \delta). \quad (48g)$$

An interaction representation is used in which the energy of state of $|1; n\rangle$ is set equal to zero for each n . The label n refers to a set of specific values for n_1, n_2, n_3, n_4 . Effects of atomic motion are neglected, but could be included easily by replacing Δ, Δ', δ , and δ' by $\tilde{\Delta}, \tilde{\Delta}', \tilde{\delta}$, and $\tilde{\delta}'$ of Sec. II.

Within the subspace generated by the basis states $|1; n\rangle, \dots, |7; n\rangle$, the Hamiltonian takes on the form shown in Table I. The entries are shown in frequency rather than energy units and the coupling constant

$$g_j = f_j(\bar{n}_j)^{1/2} \quad (49)$$

is evaluated at the average number of photons in field j , assumed to be a large number. The coupling constant g_j can be related to the Rabi frequencies of Sec. III as follows:

$$g_1 = -i\chi e^{i\mathbf{k} \cdot \mathbf{R}}, \quad g_2 = -i\chi_+ e^{i\mathbf{k}_+ \cdot \mathbf{R}}, \\ g_3 = -i\chi' e^{i\mathbf{k}' \cdot \mathbf{R}}, \quad g_4 = -i\chi'_- e^{i\mathbf{k}'_- \cdot \mathbf{R}}. \quad (50)$$

The object of the calculation is to evaluate the upper state population ρ_{33} defined as

$$\rho_{33} = \sum_{n, m, p, q} \langle 3; n, m; p, q | \rho | 3; n, m; p, q \rangle \\ = \sum_{n, n', j, j'=4}^7 \langle j; n | \rho | j'; n' \rangle, \quad (51)$$

where $\rho = |\psi\rangle\langle\psi|$ is the density operator for the system, and $|j; n\rangle$ is given in Eqs. (48d)–(48g). The second sum in Eq. (51) is restricted to values of n and n' such that the corresponding occupation numbers of states $|j; n\rangle$ and $|j'; n'\rangle$ are equal. For example, if $j=j'$, then $n_1=n'_1, n_2=n'_2, n_3=n'_3, n_4=n'_4$; if $j=4$ and $j'=6$, then $n_1-1=n'_1, n_2=n'_2-1, n_3=n'_3, n_4=n'_4$, etc. It is a straightforward calculation to find ρ_{33} using perturbation theory for the Hamiltonian of Table I. That calculation is, in effect, identical to that of the bare-atom approach. In this section, however, we wish to use a DAP in which a part of the Hamiltonian is diagonalized. Using weak-field dressed states (i.e., dressed states correct to order g_1

TABLE I. Subblock of matrix H (in frequency units) in the $|i; n_1, n_2, n_3, n_4\rangle$ basis.

	$ 1\rangle$	$ 2\rangle$	$ 3\rangle$	$ 4\rangle$	$ 5\rangle$	$ 6\rangle$	$ 7\rangle$
$\langle 1 $	0	ig_1^*	ig_2^*	0	0	0	0
$\langle 2 $	$-ig_1$	Δ	0	ig_3^*	ig_4^*	0	0
$\langle 3 $	$-ig_2$	0	$\Delta - \delta$	0	0	ig_1^*	ig_4^*
$\langle 4 $	0	$-ig_3$	0	$\Delta + \Delta'$	0	0	0
$\langle 5 $	0	$-ig_4$	0	0	$\Delta + \Delta' + \delta'$	0	0
$\langle 6 $	0	0	$-ig_3$	0	0	$\Delta + \Delta' - \delta$	0
$\langle 7 $	0	0	$-ig_4$	0	0	0	$\Delta + \Delta' + \delta' - \delta$

or g_2) defined as¹³

$$|A; n\rangle = |1; n\rangle + \theta_B |2; n\rangle + \theta_C |3; n\rangle, \quad (52a)$$

$$|B; n\rangle = -\theta_B^* |1; n\rangle + |2; n\rangle, \quad (52b)$$

$$|C; n\rangle = -\theta_C^* |1; n\rangle + |3; n\rangle, \quad (52c)$$

$$|4; n\rangle, |5; n\rangle, |6; n\rangle, |7; n\rangle \text{ as in Eq. (48),} \quad (52d)$$

where

$$\theta_B = ig_1/\Delta, \quad (53a)$$

$$\theta_C = ig_2/(\Delta - \delta), \quad (53b)$$

we replace the bare-state Hamiltonian of Table I by the corresponding dressed-state Hamiltonian H^D shown in Table II. The Hamiltonian of Table II consists of two block-diagonal sections (separated by a frequency of order $|\Delta|$) which are coupled by the atom-field interaction. The energy levels of some of the dressed states are shown in Fig. 5.

In the absence of collisions, the time evolution of the density matrix is given by

$$\dot{\tilde{\rho}} = -i[H^D, \tilde{\rho}], \quad (54)$$

where the tilde indicates the interaction representation. It follows from Eq. (54) and Table II that density-matrix elements evolve as

$$\begin{aligned} \dot{\tilde{\rho}}_{\mu_n v_{n'}} &= -i\omega_\mu \tilde{\rho}_{\mu_n v_{n'}} \\ &- i \sum_{l=4}^7 (H_{\mu l}^D \tilde{\rho}_{l_n v_{n'}} - \tilde{\rho}_{\mu_n l_n} H_{l v}^D), \\ \mu, v &= A, B, C \end{aligned} \quad (55a)$$

$$\begin{aligned} \dot{\tilde{\rho}}_{l_n v_{n'}} &= -i\omega_l \tilde{\rho}_{l_n v_{n'}} - i \sum_{\mu=A, B, C} H_{l \mu}^D \tilde{\rho}_{\mu_n v_{n'}}, \\ v &= A, B, C, \quad l = 4, 5, 6, 7, \end{aligned} \quad (55b)$$

$$\begin{aligned} \dot{\tilde{\rho}}_{l_n l_n'} &= -i\omega_{ll'} \tilde{\rho}_{l_n l_n'} \\ &- i \sum_{\mu=A, B, C} (H_{l \mu}^D \tilde{\rho}_{\mu_n l_n'} - \tilde{\rho}_{l_n \mu_n} H_{\mu l'}^D), \\ l, l' &= 4, 5, 6, 7, \end{aligned} \quad (55c)$$

where

$$\omega_{ij} = H_{ii}^D - H_{jj}^D. \quad (56)$$

It is to be noted that, neglecting variations of g_j with n ,

the subscripts n and n' which specify the quantum numbers n_1, n_2, n_3, n_4 , do not appear in matrix elements of H^D . It is assumed implicitly in Eqs. (55) that the atom-field interaction is turned on in a time that is long compared with $|\Delta|^{-1}$. With such an adiabatic turn on of the interaction, terms involving time derivatives of the field amplitudes are neglected. The initial values for density-matrix elements are those at $t = -\infty$, before any atom-field interaction. Explicitly, these initial values are

$$\begin{aligned} \tilde{\rho}_{A_n A_{n'}} &= \langle 1; n_1, n_2, n_3, n_4 | \rho | 1; n'_1, n'_2, n'_3, n'_4 \rangle = \tilde{\rho}_{nn'}^0, \\ \tilde{\rho}_{l_n j_{n'}} &= 0, \quad i, j \neq A. \end{aligned} \quad (57)$$

We are interested in a perturbation solution to Eqs. (55). Since H_{IA}^D is of order g^2 , and H_{IB}^D and H_{IC}^D are of order g^1 , one can infer from Eqs. (55) that, in order to calculate ρ_{33} to fourth order in g , we require

$$\begin{aligned} \tilde{\rho}_{ll'} &\sim O(g^4), \\ \tilde{\rho}_{l\mu} &\sim O(g^3), \\ \tilde{\rho}_{IA} &\sim O(g^2), \\ \tilde{\rho}_{\mu\nu} &\sim O(g^2), \\ \tilde{\rho}_{A\mu} &\sim O(g^1), \\ \tilde{\rho}_{AA} &\sim O(g^0), \end{aligned} \quad (58)$$

where, unless noted otherwise, we adopt the convention that

$$\begin{aligned} \mu, v &= B, C, \\ l, l' &= 4, 5, 6, 7. \end{aligned} \quad (59)$$

To this order in g , Eqs. (5) become

$$\dot{\tilde{\rho}}_{A_n A_{n'}} = 0, \quad (60a)$$

$$\dot{\tilde{\rho}}_{A_n \mu_{n'}} = -i\omega_{A\mu} \tilde{\rho}_{A_n \mu_{n'}}, \quad (60b)$$

$$\dot{\tilde{\rho}}_{\mu_n v_{n'}} = -i\omega_\mu \tilde{\rho}_{\mu_n v_{n'}}, \quad (60c)$$

$$\dot{\tilde{\rho}}_{l_n v_{n'}} = -i\omega_l \tilde{\rho}_{l_n v_{n'}} - i \sum_{\mu=A, B, C} H_{l \mu}^D \tilde{\rho}_{\mu_n v_{n'}}, \quad (60d)$$

$$\begin{aligned} \dot{\tilde{\rho}}_{l_n l_n'} &= -i\omega_{ll'} \tilde{\rho}_{l_n l_n'} \\ &- i \sum_{\mu=A, B, C} (H_{l \mu}^D \tilde{\rho}_{\mu_n l_n'} - \tilde{\rho}_{l_n \mu_n} H_{\mu l'}^D), \end{aligned} \quad (60e)$$

TABLE II. Subblock of matrix H^D (in frequency units) in the dressed basis.

	$ A\rangle$	$ B\rangle$	$ C\rangle$	$ 4\rangle$	$ 5\rangle$	$ 6\rangle$	$ 7\rangle$
$\langle A $	0	0	0	$i\theta_B^* g_3^*$	$i\theta_B^* g_4^*$	$i\theta_C^* g_3^*$	$i\theta_C^* g_4^*$
$\langle B $	0	Δ	0	ig_3^*	ig_4^*	0	0
$\langle C $	0	0	$\Delta - \delta$	0	0	ig_3^*	ig_4^*
$\langle 4 $	$-i\theta_B g_3$	$-ig_3$	0	$\Delta + \Delta'$	0	0	0
$\langle 5 $	$-i\theta_B g_4$	$-ig_4$	0	0	$\Delta + \Delta' + \delta'$	0	0
$\langle 6 $	$-i\theta_C g_3$	0	$-ig_3$	0	0	$\Delta + \Delta' - \delta$	0
$\langle 7 $	$-i\theta_C g_4$	0	$-ig_4$	0	0	0	$\Delta + \Delta' + \delta' - \delta$

$$\tilde{\rho}_{ij} = \tilde{\rho}_{ji}^*, \quad (60f)$$

with initial conditions

$$\tilde{\rho}_{A_n A_{n'}} = \tilde{\rho}_{nn'}^0 \text{ all other } \tilde{\rho}_{ij} = 0. \quad (60g)$$

Relaxation must now be incorporated into Eqs. (60). In the bare-atom picture, relaxation is accounted for simply by writing

$$(\partial \tilde{\rho}_{ij}^B / \partial t)_{\text{relax}} = -(\gamma_{ij} + \Gamma_{ij}) \tilde{\rho}_{ij}^B = -\gamma_{ij}^t \tilde{\rho}_{ij}^B, \quad \Gamma_{ii} = 0, \quad \gamma_1 = 0. \quad (61)$$

In the bare-atom picture, collisions and spontaneous emission result in a decay of the various density-matrix elements, but no coupling between density-matrix elements (collisions are not energetic enough to couple the bare states and the repopulation of states 1 and 2 via spontaneous-emission results in contributions to ρ_{33} of order higher than g^4). On the other hand, collisions and spontaneous emission will lead to coupling of dressed-state density-matrix elements. To arrive at the relaxation equations in the DAP, (i) Eqs. (52) are used to write dressed density-matrix elements $\tilde{\rho}_{ij}^D$ in terms of the bare ones $\tilde{\rho}_{ij}^B$; (ii) Eq. (61) is used to write the $\tilde{\rho}_{ij}^B$ in terms of the $\tilde{\rho}_{ij}^D$, and (iii) the inverse of Eqs. (52) is used to reexpress the $\tilde{\rho}_{ij}^B$ in terms of the $\tilde{\rho}_{ij}^D$. When this procedure is carried out, the resultant expressions are very complicated.¹⁴ However, in the perturbation theory limit of Eq. (58), they take the relatively simple form

$$(\partial \tilde{\rho}_{A_n A_{n'}} / \partial t)_{\text{relax}} = 0, \quad (62a)$$

$$(\partial \tilde{\rho}_{A_n \mu_{n'}} / \partial t)_{\text{relax}} = -\gamma_{12} \tilde{\rho}_{A_n \mu_{n'}} - \theta_\mu^* \gamma_{12}^t \tilde{\rho}_{A_n A_{n'}}, \quad (62b)$$

$$(\partial \tilde{\rho}_{\mu_n \nu_{n'}} / \partial t)_{\text{relax}} = 2\theta_\mu \theta_v^* \Gamma_{12} \tilde{\rho}_{A_n A_{n'}} - \gamma_2 \tilde{\rho}_{\mu_n \nu_{n'}} + (\gamma_{12}^t - \gamma_2) (\theta_v^* \tilde{\rho}_{\mu_n A_{n'}} + \theta_\mu \tilde{\rho}_{A_n \nu_{n'}}), \quad (62c)$$

$$(\partial \tilde{\rho}_{l_n A_{n'}} / \partial t)_{\text{relax}} = -\gamma_{13}^t \tilde{\rho}_{l_n A_{n'}}, \quad (62d)$$

$$(\partial \tilde{\rho}_{l_n \mu_{n'}} / \partial t)_{\text{relax}} = -\gamma_{23}^t \tilde{\rho}_{l_n \mu_{n'}} + (\gamma_{13}^t - \gamma_{23}^t) \theta_\mu^* \tilde{\rho}_{l_n A_{n'}}, \quad (62e)$$

$$(\partial \tilde{\rho}_{l_n l_{n'}} / \partial t)_{\text{relax}} = -\gamma_3 \tilde{\rho}_{l_n l_{n'}}. \quad (62f)$$

Equations (60) and (62) are now combined and the following steady-state solutions are obtained:

$$\tilde{\rho}_{A_n A_{n'}} = \tilde{\rho}_{nn'}^0, \quad (63a)$$

$$\tilde{\rho}_{A_n \mu_{n'}} = \left[-\frac{\theta_\mu^* \gamma_{12}^t \tilde{\rho}_{nn'}^0}{\gamma_{12}^t + i\omega_{A\mu}} \right], \quad (63b)$$

$$\tilde{\rho}_{\mu_n \nu_{n'}} = -\frac{2\theta_\mu \theta_v^* \Gamma_{12} \tilde{\rho}_{nn'}^0}{\gamma_2 + i\omega_{\mu\nu}} + [(\gamma_{12}^t - \gamma_2) (\theta_v^* \tilde{\rho}_{\mu_n A_{n'}} + \theta_\mu \tilde{\rho}_{A_n \nu_{n'}})], \quad (63c)$$

$$\tilde{\rho}_{l_n A_{n'}} = -\frac{i H_{IA}^D \tilde{\rho}_{nn'}^0}{\gamma_{13}^t + i\omega_{IA}} + \left[-i \sum_{\mu=B,C} \frac{H_{l\mu}^D \tilde{\rho}_{\mu_n A_{n'}}}{\gamma_{23}^t + i\omega_{l\mu}} \right], \quad (63d)$$

$$\tilde{\rho}_{l_n \mu_{n'}} = -i \sum_{v=B,C} \frac{H_{lv}^D \tilde{\rho}_{\nu_n \mu_{n'}}}{\gamma_{23}^t + i\omega_{lv}} + \left[-\frac{H_{IA}^D \tilde{\rho}_{A_n \mu_{n'}}}{\gamma_{23}^t + i\omega_{IA}} \right], \quad (63e)$$

$$\tilde{\rho}_{l_n l_{n'}} = -i \sum_{\alpha=A,B,C} \frac{H_{la}^D \tilde{\rho}_{a_n l_{n'}} - \tilde{\rho}_{l_n a_n} H_{al}^D}{\gamma_3 + i\omega_{ll'}}. \quad (63f)$$

These equations are exactly equivalent to Eqs. (34) and lead to exactly the same results obtained in Eq. (38).

Although Eqs. (63) are "exact" (in the perturbation theory limit), they are clearly more complicated than the corresponding equations in the BAP. It is known that DAP expressions simplify significantly in the so-called secular approximation,^{9,10} that is, when

$$\gamma_{12}^t \ll |\Delta|. \quad (64)$$

In that limit all the terms in square brackets in Eq. (63) can be dropped to lowest order in γ_{12}^t / Δ , and one obtains the simplified equations

$$\tilde{\rho}_{A_n \mu_{n'}} \simeq 0, \quad (65a)$$

$$\tilde{\rho}_{\mu_n \nu_{n'}} = \frac{2\theta_\mu \theta_v^* \Gamma_{12} \tilde{\rho}_{nn'}^0}{\gamma_2 + i\omega_{\mu\nu}}, \quad (65b)$$

$$\tilde{\rho}_{l_n A_{n'}} = -\frac{i H_{IA}^D \tilde{\rho}_{nn'}^0}{\gamma_{13}^t + i\omega_{IA}}, \quad (65c)$$

$$\tilde{\rho}_{l_n \mu_{n'}} = -\sum_{v=B,C} \frac{H_{lv}^D \tilde{\rho}_{\nu_n \mu_{n'}}}{\gamma_{23}^t + i\omega_{lv}}, \quad (65d)$$

$$\tilde{\rho}_{l_n l_{n'}} = -i \sum_{\alpha=A,B,C} \frac{H_{la}^D \tilde{\rho}_{a_n l_{n'}} - \tilde{\rho}_{l_n a_n} H_{al}^D}{\gamma_3 + i\omega_{ll'}}. \quad (65e)$$

In this form, the role of collisions is readily apparent. In the absence of collisions ($\Gamma_i = 0$), $\tilde{\rho}_{BB} = \tilde{\rho}_{CC} = \tilde{\rho}_{BC} = \tilde{\rho}_{CB} = 0$ [Eq. (65b)]. Consequently, $\tilde{\rho}_{IB} = \tilde{\rho}_{IC} = 0$ from Eq. (65d) and only $\tilde{\rho}_{IA}$, corresponding to the two-photon resonance, contributes to $\tilde{\rho}_{ll'}$ in Eq. (65e). Thus, in the DAP, the absence of CARE- and PIER4-type resonances can be attributed to the fact that states $|B\rangle$ and $|C\rangle$ are not populated when collisions do not occur. The fact that $\tilde{\rho}_{\mu\nu} = 0$ ($\mu, \nu = B, C$) in the absence of collisions can be connected with energy conservation—there is no mechanism to compensate for the energy defect $\hbar\Delta$ between states $|A\rangle$ and $|B\rangle$ (or $|C\rangle$). Collisions possess frequency components (of order of the inverse collision duration) to drive the $A \rightarrow B, C$ transitions.

As a specific example, we evaluate Eqs. (65) for the

same set of parameters used in arriving at Eq. (38) of Sec. III. We set $\delta' = \delta$ and $\kappa = -\kappa'$, and consider only the component of $\bar{\rho}_{I_n I'_n}$, which varies as $\chi\chi^* + \chi'\chi'^*$ (or, equivalently, as $g_1 g_2^* g_3 g_4^*$) or its conjugate. From Eqs. (65) and Table II, it follows that $\bar{\rho}_{4_n 7_n}$ and $\bar{\rho}_{7_n 4_n}$ have this χ dependence. In the interaction representation that was chosen, an energy $\sum_{i=1}^4 \hbar n_i \Omega_i$ was subtracted from each

nearly degenerate subblock of H^D . This implies that the total density-matrix elements are related to those of the interaction representation by

$$\rho_{I_n I'_n}(t) = \bar{\rho}_{I_n I'_n} \exp \left[-i \sum_{j=1}^4 (n_j - n'_j) \Omega_j t \right]. \quad (66)$$

Using Eqs. (66), (48d), (48g), and (47), one can write

$$\begin{aligned} \rho_{4_n 7_n}(t) = & \langle 3; n_1 - 1, n_2; n_3 - 1, n_4 | \rho | 3; n'_1, n'_2 - 1; n'_3, n'_4 - 1 \rangle \\ & \times \exp \{ -i[(n_1 - n'_1)\Omega + (n_2 - n'_2)(\Omega + \delta) + (n_3 - n'_3)\Omega' + (n_4 - n'_4)(\Omega' - \delta')]t \}, \end{aligned} \quad (67)$$

with an analogous equation for ρ_{74} . In calculating the contribution to ρ_{33} from Eqs. (67) and (51), one must take only those terms which are diagonal in the photon numbers, that is, terms for which

$$n'_1 = n_1 - 1, \quad n'_2 = n_2 + 1, \quad n'_3 = n_3 - 1, \quad n'_4 = n_4 + 1. \quad (68)$$

For these values of n and n' , the phase factor in Eq. (67) vanishes identically when $\delta = \delta'$. Consequently, the contribution to ρ_{33} from ρ_{47} and ρ_{74} , denoted by $S(\delta)$ as in Sec. III, is given by

$$S(\delta) = \sum_{\substack{n_1, n_2, n_3, n_4 \\ n'_1, n'_2, n'_3, n'_4}} (\bar{\rho}_{4_n 7_n} \delta_{n'_1, n_1 - 1} \delta_{n'_2, n_2 + 1} \delta_{n'_3, n_3 - 1} \delta_{n'_4, n_4 + 1}) + \text{c.c.} \quad (69)$$

Using Eqs. (65) and (50) and Table II, one can obtain

$$S(\delta) = \frac{\chi\chi^* + \chi'\chi'^*}{\gamma_3 \Delta(\Delta - \delta)} \left[2\Gamma_{12} \left[1 + \frac{\gamma_3 + 2\Gamma_{23}}{\gamma_2 + i\delta} \right] \frac{1}{[\gamma'_{23} + i(\Delta' - \delta)](\gamma'_{23} - i\Delta')} + \frac{\gamma_3 + 2\Gamma_{13}}{(\gamma'_{13})^2 + (\Delta + \Delta')^2} \right] \langle \rho^0 \rangle + \text{c.c.}, \quad (70)$$

where

$$\begin{aligned} \langle \rho^0 \rangle = & \sum_{n_1, n_2, n_3, n_4} \langle n_1 | \rho_1^0 | n_1 - 1 \rangle \langle n_2 | \rho_2^0 | n_2 + 1 \rangle \\ & \times \langle n_3 | \rho_3^0 | n_3 - 1 \rangle \langle n_4 | \rho_4^0 | n_4 + 1 \rangle \end{aligned} \quad (71)$$

and ρ^0 is the free-field density matrix for field i .¹⁵

There are two points we wish to note concerning Eq. (70). First, we see that it reproduces all but the last term of Eq. (38). The last term of Eq. (38) corresponds to a nonsecular term in the DAP which is not included in the secular approximation to the DAP, Eqs. (65) [this term is included in the full DAP equations (63)]. The nonsecular term is negligible if one has $(\Delta + \Delta') \approx 0$ or $\Delta' \approx 0$, but would be comparable to the other terms if both $|\Delta + \Delta'| \gg k u$ and $|\Delta'| \gg k' u$. Second, it is interesting to note the dependence on photon statistics given in Eq. (71). For coherent states of each field, the average density matrix $\langle \rho^0 \rangle$ is equal to unity. However, if even one of the fields has a total random phase (i.e., one field is in a pure number state), $\langle \rho^0 \rangle$ vanishes. As mentioned in Sec. III, the fields must be relatively coherent for a nonvanishing $S(\delta)$.

Thus, from either a bare- or dressed-atom approach, we arrive at the same result—only the two-photon resonance is present in the absence of collisions. The DAP offers a unified picture of the pressure-induced resonances—CARE-type resonances result from collision-induced population of dressed states $|B\rangle$ and $|C\rangle$, while PIER4-type resonances, centered at $\delta = 0$, result from collision-induced creation of the ρ_{BC} coherence.

There remains one fly in the ointment, however. Populations ρ_{BB} and ρ_{CC} , as well as coherence ρ_{BC} , are not exactly zero in the absence of collisions owing to contributions from nonsecular terms arising from spontaneous emission. These nonsecular terms would lead to CARE- or PIER4-type resonances, even in the absence of collisions, terms which are known to vanish identically from Sec. III. Of course, if one solved the full set of DAP equations (63), he would find that these terms vanish as a result of interference of various pathways in the perturbation calculation. However, the simple interpretation in terms of the DAP would be tarnished somewhat by these nonsecular terms. The situation can be remedied if complex dressed states are introduced (see Appendix). In that case, one can show that ρ_{BB} , ρ_{CC} , and ρ_{AB} are identically zero in the absence of collisions—the simple interpretation of the DAP is retained.

V. SUMMARY

By studying a three-level atom interacting with four radiation fields, we have shown how both collisionally aided radiative excitation (CARE) and pressure-induced extra resonances in four-wave mixing (PIER4) can be explained in a unified manner. Using both a bare-atom picture (BAP) and dressed-atom picture (DAP) of the reaction, we were able to argue that both types of pressure-induced extra resonances (PIER) could be explained on the basis of conservation of energy. In particular, we have found the DAP to be a convenient vehicle for viewing these pressure-induced effects.

In the near future, we plan to extend this work in two directions. First, using both the BAP and a new, semi-classical dressed-atom approach, we will calculate PIER signals arising in (i) fluorescence beats, (ii) a "four-level" atom interacting with four radiation fields, and (iii) two-photon ionization. Second, we will use both the quantized and semiclassical DAP to reanalyze pressure-induced effects produced in four-wave mixing on a "two-level" atom.

ACKNOWLEDGMENTS

This research is supported, in part, by a National Science Foundation (NSF) International Grant (No. INT 8413300). The research of P.R.B. is supported by the U. S. Office of Naval Research and the National Science Foundation (Grant No. PHY-8415781). The Laboratoire de Spectroscopie Hertzienne de l'Ecole Normale Supérieure is "associé au Centre National de la Recherche Scientifique."

APPENDIX: COMPLEX DRESSED STATES

As discussed in Sec. IV, it would be more satisfactory if dressed-state populations ρ_{BB} and ρ_{CC} vanished identically in the absence of collisions, not only in the secular approximation. It is possible to arrange for this to occur if "complex" dressed states are used. To illustrate the concepts, we consider a two-level atom interacting with a single quantized field (e.g., field 1 of Sec. IV). In the absence of collisions, the state amplitudes a_1 and a_2 for states $|1;n\rangle$ and $|2;n-1\rangle$, respectively, evolve as

$$ia_1 = ig_1^* a_2, \quad (A1a)$$

$$ia_2 = -i(\gamma_2/2)a_2 + \Delta a_2 - ig_1 a_1, \quad (A1b)$$

where the energy of state $|1;n\rangle$ has been set equal to zero. These equations imply that a complex Hamiltonian (in frequency units)

$$H = \begin{bmatrix} 0 & ig_1^* \\ -ig_1 & \Delta - \frac{1}{2}i\gamma_2 \end{bmatrix} \quad (A2)$$

can be introduced for which

$$ia_j = \sum_{l=1}^2 H_{jl} a_l, \quad j = 1, 2. \quad (A3)$$

We now define complex dressed states (CDS's) as eigenstates of H . In the spirit of the perturbative calculation of this paper, the CDS's are obtained to first order in g_1 , but, in principle, the CDS's can be defined for arbitrary g_1 . Since H is non-Hermitian, some care must be exercised.¹⁶

Let $|A^c\rangle$ and $|B^c\rangle$ be eigenkets of H . Since H is not Hermitian, $\langle A^c | B^c \rangle \neq 0$, in general. Define $|\bar{A}^c\rangle$, $|\bar{B}^c\rangle$ as eigenkets of H^\dagger , having eigenvalues which are the complex conjugates of those of states $|A^c\rangle$ and $|B^c\rangle$. In other words,

$$H|\alpha^c\rangle = \omega_\alpha^c |\alpha^c\rangle, \quad (A4)$$

$$H^\dagger |\bar{\alpha}^c\rangle = \omega_\alpha^c |\bar{\alpha}^c\rangle, \quad \alpha = A, B.$$

The eigenkets of H and H^\dagger form an orthonormal set¹⁶

$$\langle A^c | \bar{A}^c \rangle = \langle B^c | \bar{B}^c \rangle = 1,$$

$$\langle A^c | \bar{B}^c \rangle = \langle B | \bar{A}^c \rangle = 0. \quad (A5)$$

To lowest order in the fields, the eigenkets and eigenfrequencies of H and H^\dagger are

$$|A^c\rangle = |1\rangle + \varphi_B |2\rangle, \quad |B^c\rangle = |2\rangle - \bar{\varphi}_B^* |1\rangle \quad (A6a)$$

$$|\bar{A}^c\rangle = |\bar{1}\rangle + \bar{\varphi}_B |\bar{2}\rangle, \quad |\bar{B}^c\rangle = |\bar{2}\rangle - \varphi_B^* |\bar{1}\rangle \quad (A6b)$$

$$\omega_A^c = \omega_{\bar{A}}^c = 0, \quad \omega_B^c = \omega_{\bar{B}}^c = (\Delta - \frac{1}{2}i\gamma_2) \quad (A7)$$

where

$$\varphi_B = \frac{ig_1}{\Delta - \frac{1}{2}i\gamma_2}, \quad \bar{\varphi}_B = \frac{ig_1}{\Delta + \frac{1}{2}i\gamma_2} \quad (A8)$$

and $|1\rangle, |2\rangle$ and $|\bar{1}\rangle, |\bar{2}\rangle$ are eigenkets of H and H^\dagger , respectively, in the absence of the applied field. Note that $\varphi_B \sim \theta_B$ [Eq. (53a)] when $\gamma_2 \sim 0$.

An arbitrary ket $|\psi\rangle$ is expanded (in the interaction representation) as

$$|\tilde{\psi}\rangle = \tilde{a}_A^c |A^c\rangle + \tilde{a}_B^c |B^c\rangle, \quad (A9)$$

where

$$\tilde{a}_\alpha^c = \langle \bar{\alpha}^c | \tilde{\psi} \rangle, \quad \alpha = A, B. \quad (A10)$$

The density matrix (in the interaction representation) is defined as

$$\tilde{\rho} = |\tilde{\psi}\rangle \langle \tilde{\psi}|, \quad (A11)$$

with density matrix elements in the complex basis $\tilde{\rho}_{\alpha\beta}^c$ defined by

$$\tilde{\rho}_{\alpha\beta}^c = \langle \bar{\alpha}^c | \tilde{\psi} \rangle \langle \tilde{\psi} | \bar{\beta}^c \rangle. \quad (A12)$$

The time evolution of density matrix elements is obtained from $\dot{\tilde{\rho}} = (i\hbar)^{-1} (H\tilde{\rho} - \tilde{\rho}H^\dagger)$. Taking matrix elements as in (A12), one finds

$$\dot{\tilde{\rho}}_{\alpha\beta}^c = -i \sum_{\lambda} [H_{\bar{\alpha}\lambda} \tilde{\rho}_{\lambda\beta}^c - \tilde{\rho}_{\alpha\lambda}^c (H_{\bar{\beta}\lambda})^*], \quad (A13)$$

where the completeness relation, $\sum |\alpha^c\rangle \langle \bar{\alpha}^c| = 1$, has been used. Defining a complex dressed Hamiltonian H_c^D as one having matrix elements between states $\langle \bar{\alpha}^c |$ and $|\alpha^c\rangle$, one can use Eqs. (A2) and (A6) to write

$$H_c^D = \begin{bmatrix} 0 & 0 \\ 0 & \Delta - \frac{1}{2}i\gamma_2 \end{bmatrix}. \quad (A14)$$

From Eqs. (A13) and (A14), it immediately follows that

$$\dot{\tilde{\rho}}_{AA}^c = 0, \quad (A15a)$$

$$\dot{\tilde{\rho}}_{AB}^c = \dot{\tilde{\rho}}_{BA}^{c*} = -(\frac{1}{2}\gamma_2 - i\Delta) \tilde{\rho}_{AB}^c, \quad (A15b)$$

$$\dot{\tilde{\rho}}_{BB}^c = -\gamma_2 \tilde{\rho}_{BB}^c, \quad (A15c)$$

subject to the initial conditions

$$\tilde{\rho}_{AA}^{c_0} = 1, \quad \tilde{\rho}_{AB}^{c_0} = \tilde{\rho}_{BA}^{c_0} = \tilde{\rho}_{BB}^{c_0} = 0. \quad (A16)$$

In the absence of collisions, but including spontaneous

emission, $\rho_{BB}^c = \rho_{AB}^c = \rho_{BA}^c = 0$ in this complex dressed-state basis. It remains to include collisional relaxation in Eqs. (A15). The procedure for carrying this out is outlined in Sec. IV. In terms of the complex dressed states, one finds, to the order indicated in Eq. (58),

$$\dot{\rho}_{AA}^c = 0, \quad (A17a)$$

$$\dot{\rho}_{AB}^c = -(\frac{1}{2}\gamma_2 - i\Delta)\rho_{AB}^c - \Gamma_{12}\varphi_B^*\rho_{AA}^c, \quad (A17b)$$

$$\begin{aligned} \dot{\rho}_{BB}^c = & -\gamma_2\rho_{BB}^c + \Gamma_{12}(\varphi_B\rho_{AB}^c + \varphi_B^*\rho_{BA}^c) \\ & + 2|\varphi_B|^2\Gamma_{12}\rho_{AA}^c. \end{aligned} \quad (A17c)$$

These equations can now be generalized to the three-level problem of the main text. The Hamiltonian $H^D(\theta)$ of Table II can be replaced by $H^{Dc}(\varphi)$ in which the θ_μ of Eq. (53) are replaced by

$$\varphi_\mu = \frac{ig_\mu}{\Delta - \frac{1}{2}i\gamma_2}, \quad \mu = B, C \quad (A18a)$$

and the θ_μ^* of Eq. (53) are replaced by

$$\bar{\varphi}_\mu^* = \frac{-ig_\mu^*}{\Delta - \frac{1}{2}i\gamma_2}, \quad \mu = B, C. \quad (A18b)$$

Using Eq. (A13), one can show that the steady-state solutions analogous to Eqs. (63), correct to the order of Eqs. (56), are

$$\tilde{\rho}_{A_n A_{n'}}^c = \tilde{\rho}_{nn'}^0, \quad (A19a)$$

$$\tilde{\rho}_{A_n \mu_{n'}}^c = -\frac{\bar{\varphi}_\mu^* \Gamma_{12} \tilde{\rho}_{nn'}^0}{\gamma_{12}^t + i\omega_{A_\mu}}, \quad (A19b)$$

$$\tilde{\rho}_{\mu_n v_{n'}}^c = \frac{2\varphi_\mu \bar{\varphi}_v^* \Gamma_{12} \tilde{\rho}_{nn'}^0}{\gamma_2 + i\omega_{\mu v}} + \Gamma_{12}(\bar{\varphi}_v \tilde{\rho}_{\mu_n A_{n'}}^c + \varphi_\mu \tilde{\rho}_{A_n v_{n'}}^c), \quad (A19c)$$

$$\tilde{\rho}_{l_n A_{n'}}^c = -\frac{iH_{IA}^{Dc} \tilde{\rho}_{nn'}^0}{\gamma_{13}^t + i\omega_{IA}} - i \sum_{\mu=B,C} \frac{H_{l_\mu}^{Dc} \tilde{\rho}_{\mu_n A_{n'}}^c}{\gamma_{13}^t + i\omega_{l_\mu}}, \quad (A19d)$$

$$\tilde{\rho}_{l_n \mu_{n'}}^c = -i \sum_{v=B,C} \left[\frac{H_{lv}^{Dc} \tilde{\rho}_{v_n \mu_{n'}}^c}{\gamma_{23}^t + i\omega_{l_\mu}} \right] - \frac{H_{IA}^{Dc} \tilde{\rho}_{A_n \mu_{n'}}^c}{\gamma_{23}^t + i\omega_{l_\mu}}, \quad (A19e)$$

$$\tilde{\rho}_{l_n l_{n'}}^c = -i \sum_{a=A,B,C} \frac{H_{l_a}^{Dc} \tilde{\rho}_{a_n l_{n'}}^c - \tilde{\rho}_{l_n a_{n'}}^c (H_{l_a}^{Dc})^*}{\gamma_3 + i\omega_{l_a}}, \quad (A19f)$$

where ω_{ij} is still defined by Eq. (56). In the absence of collisions ($\Gamma_{ij} = 0$), $\rho_{A_\mu}^c$ and $\rho_{\mu_n}^c$ ($\mu, v = B, C$) are identically zero. Consequently, $\rho_{IB}^c = \rho_{IC}^c = 0$, and the sole contribution to ρ_{33} arises from the two-quantum resonances. With collisions present, both the stepwise and two-quantum resonances contribute. In the absence of collisions, the vanishing of $\rho_{\mu v}$ ($\mu, v = BC$) is no longer restricted to the secular approximation.¹⁷

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²See, for example, A. Gallagher and T. Holstein, *Phys. Rev. A* **16**, 2413 (1977).

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⁹See, for example, C. Cohen-Tannoudji, in *Frontiers in Laser Spectroscopy*, edited by R. Balian, S. Haroche, and S. Liberman (North-Holland, Amsterdam, 1977), pp. 3–104, and references therein; S. Reynaud and C. Cohen Tannoudji, *J. Phys.* **43**, 1021 (1982).

¹⁰G. Grynberg, *J. Phys. B* **14**, 2089 (1981).

¹¹Additional resonances also occur at $\Omega' + \delta = \omega'$ and $\Omega' - 2\delta = \omega'$, but these can be eliminated by a proper choice of the various wave vectors (see Secs. III and IV).

¹²At low pressure, one finds an additional resonance centered at $\delta = 0$ when Eq. (43) is integrated over velocity. This resonance has width $2\gamma_{23}^t$ and its relative amplitude decreases with increasing pressure. To eliminate this additional resonance altogether, one can choose the detuning $|\Delta'|$ to be much greater than the Doppler width $k'u$, at the cost of reduced signal.

¹³The dressed states (52b) and (52c) are not strictly correct, even to first order in g_1 and g_2 . A term $-\theta_c^*|1; n_1 - 1, n_2 + 1; n_3, n_4\rangle$ should be added to Eq. (52b) and a term $-\theta_c^*|1; n_1 + 1, n_2 - 1; n_3, n_4\rangle$ to Eq. (52c). It then follows that $|B; n_1, n_2; n_3, n_4\rangle = |C; n_1 - 1, n_2 + 1; n_3, n_4\rangle$ and that all the dressed states can be labeled simply by $|A; n_1, n_2; n_3, n_4\rangle$, $|B; n'_1, n'_2; n_3, n_4\rangle$, for arbitrary n_1, n_2, n'_1, n'_2 which satisfy $n_1 + n_2 = n'_1 + n'_2$. The equations of the text are unaltered if these “correct” dressed states are used. The physical argu-

ments given in this paper are based implicitly on a transition from an initial density-matrix element

$$\langle 1; n_1, n_2; n_3, n_4 | \rho | 1; n_1, n_2; n_3, n_4 \rangle$$

to a final-state density-matrix element

$$\langle 3; n_1 - 1, n_2; n_3 - 1, n_4 | \rho | 3; n_1, n_2 - 1; n_3, n_4 - 1 \rangle .$$

Such a final-state density-matrix element does *not* contribute to the final state population ρ_{33} . To be rigorously correct, the physical arguments should be based on a transition from an initial-state *coherence*

$$\langle 1; n_1 + 1, n_2; n_3 + 1, n_4 | \rho | 1; n_1, n_2 + 1; n_3, n_4 + 1 \rangle$$

to a final-state population

$$\langle 3; n_1, n_2; n_3, n_4 | \rho | 3; n_1, n_2; n_3, n_4 \rangle .$$

Mathematically, the two approaches can be mapped into one another. We have chosen the first method to explain the results since the physical arguments can be presented in a somewhat simpler fashion using that method.

¹⁴P. R. Berman and R. Salomaa, Phys. Rev. A **25**, 2667 (1982).

¹⁵The χ 's appearing in Eq. (70) have no n dependence since the g 's have been defined at $n = \bar{n}$ [Eq. (49)] on the assumption that \bar{n} is large for each mode. The n dependence of the χ 's could be included by using Eqs. (49) and (50) with \bar{n} set back equal to n in Eq. (49).

¹⁶P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), pp. 884–886.

¹⁷Complex dressed states have also been used to calculate the collision-induced Rayleigh gain for an ensemble of two-level atoms; H. Friedman and A. D. Wilson-Gordon, in *Advances in Laser Science III*, edited by A. C. Tam, J. L. Gole, and W. C. Stwalley (AIP, New York, 1988), pp. 121–129.